# Science, Application, Monitoring, and Illustrative Case Studies of Biogeochemical Remediaiton

Sixth International Symposium on Bioremediation and Sustainable Environmental Technologies

May 11, 2023

microbialinsights

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OREGON HEALTH & SCIENCE UNIVERSITY

EVONIK
Leading Beyond Chemistry

# Panel Discussion Format

- Five panelists for the following topics:
  - Science
  - Design
  - Application
  - Monitoring
  - Example Case Studies

- 100 minutes for the Panel

- Discussion is divided into two sections:

1. Each panelist gets ~10-15 minutes (~60-70 minutes)
   - 7-10 minutes to present on their topic
   - 3-5 minutes for Q&A for that topic

2. Open Discussion (~30-40 minutes)
   - Questions from the audience

Science

**Prof. Paul G. Tratnyek** (*Oregon Health & Science University*)

- Aquatic redox chemistry
- Environmental fate and remediation/treatment of contaminants
- Contaminant reduction by zerovalent iron (ZVI, nZVI, PRBs)
- In situ chemical reduction (ISCR) and oxidation (ISCO)

Design

**Alan Seech, Ph.D.**

- M.Sc. (Soil Chemistry) and Ph.D. (Environmental Microbiology), University of Guelph, Canada
- Focus on remediation of soil and groundwater contaminated with chlorinated pesticides and heavy metals
- First of five US patents on combination of biodegradable organic carbon with ZVI issued in 1995

Application

**Eric Moskal**

- Technical Expert |Cascade Remediation
- Expertise in pneumatic and hydraulic emplacement of reagents

Monitoring

**Dora Taggert**

CEO | Microbial Insights
Biomedical Engineering degree Vanderbilt University

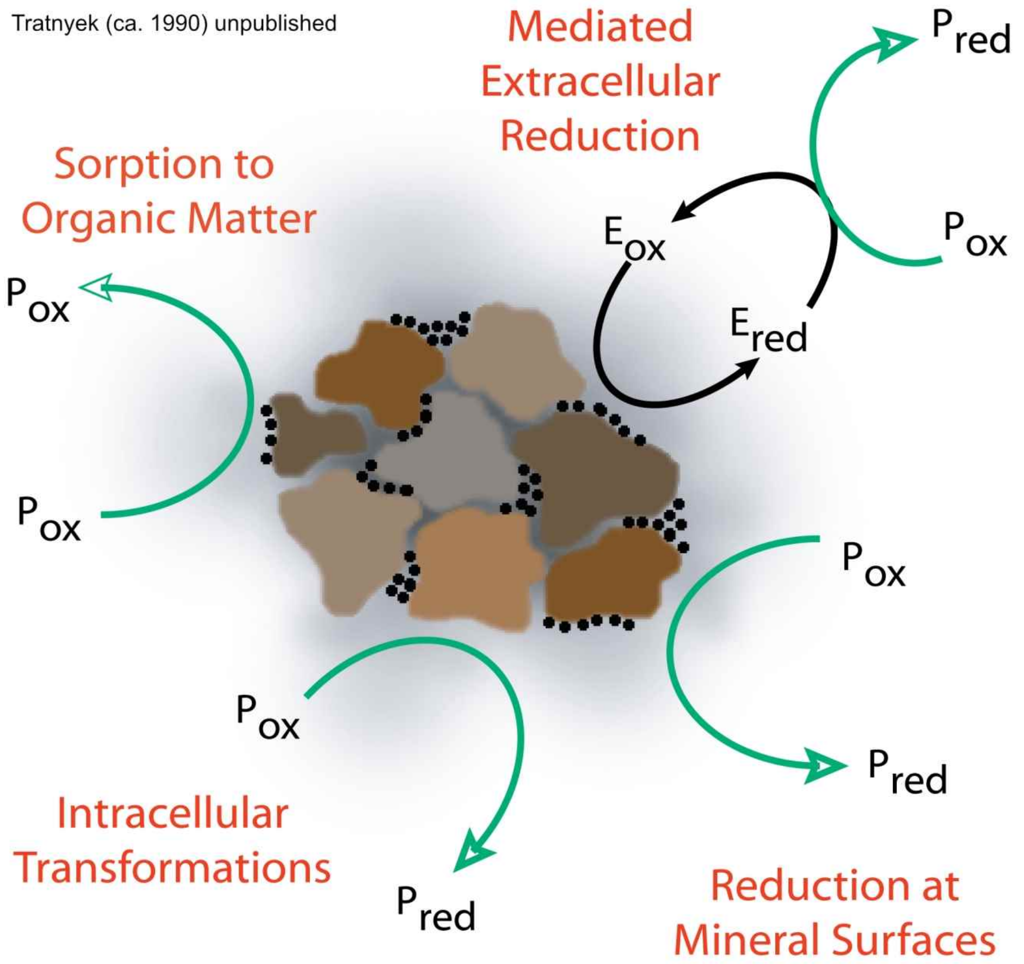
Illustrative Case Studies

**Daniel Leigh, P.G., CH.G.**

- Technology Leader for Bioremediation and Chemical Reduction
- Over 30 years of experience designing, bench testing, and implementing remediation technologies

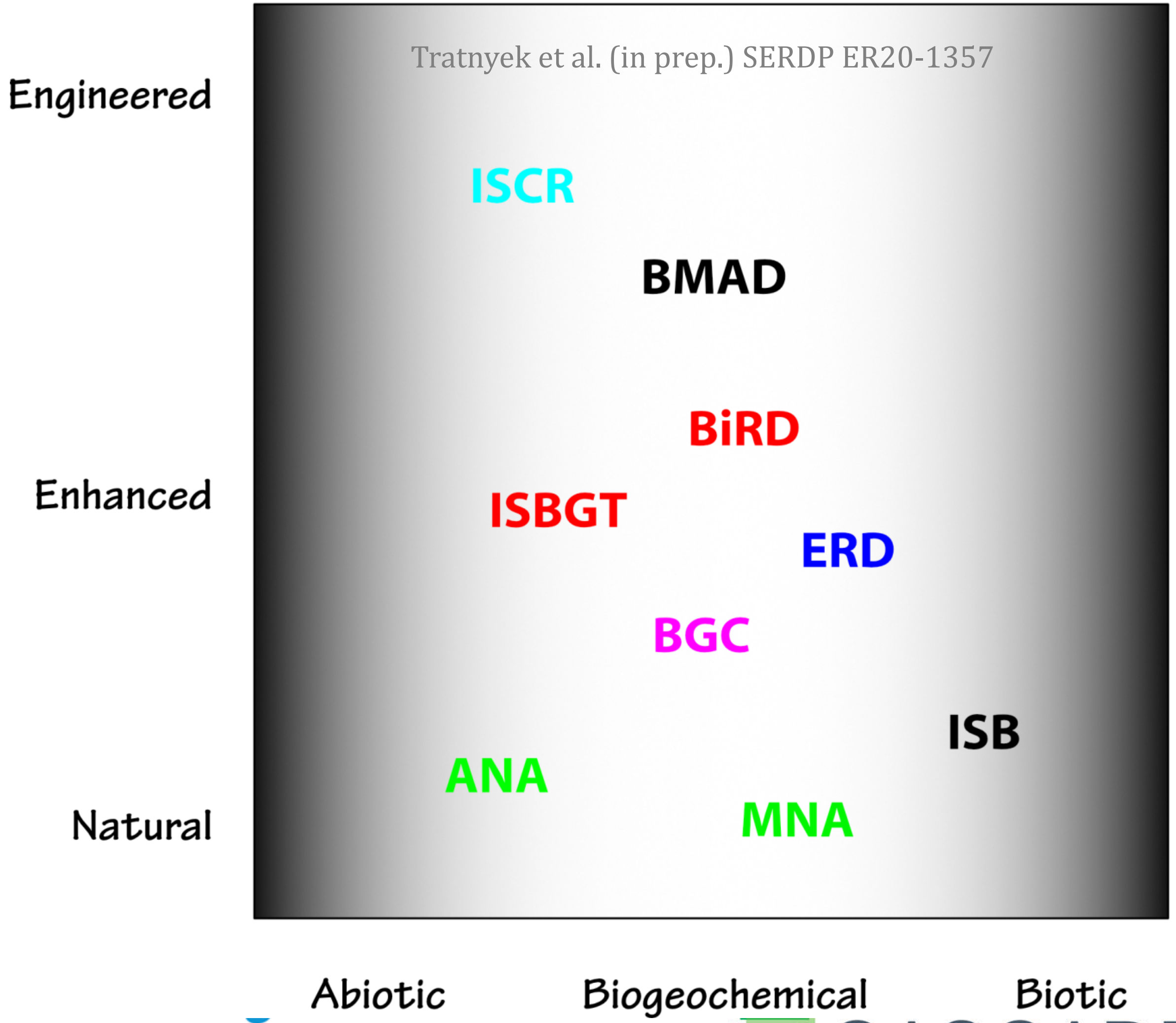
# Fundamental Science behind Biogeochemical Remediation

Professor Paul Tratynek
Oregon Health & Science University


Tratnyek (ca. 1990) unpublished

# Biogeochemical Remediation

## And variations thereof



- **ISCR** (Seech):
  In situ chemical reduction
- **BMAD** (Scherer):
  Biologically Mediated Abiotic Degradation
- **ISRM** (Fruchter):
  In situ redox manipulation
- **BiRD** (Kennedy):
  Biogeochemical Reductive Dechlorination
- **ISBGT** (Evans):
  In Situ Biogeochemical Transformation
- **BGC** (Leigh):
  Biogeochemical Remediation
- **(A)(M)NA** (Wilson)
  (Abiotic) (Monitored) Natural Attenuation
- **ERD** (EVO folks)
  Enhanced Reductive Dechlorination
- **ISB** (Freedman)
  In Situ Bioremediation

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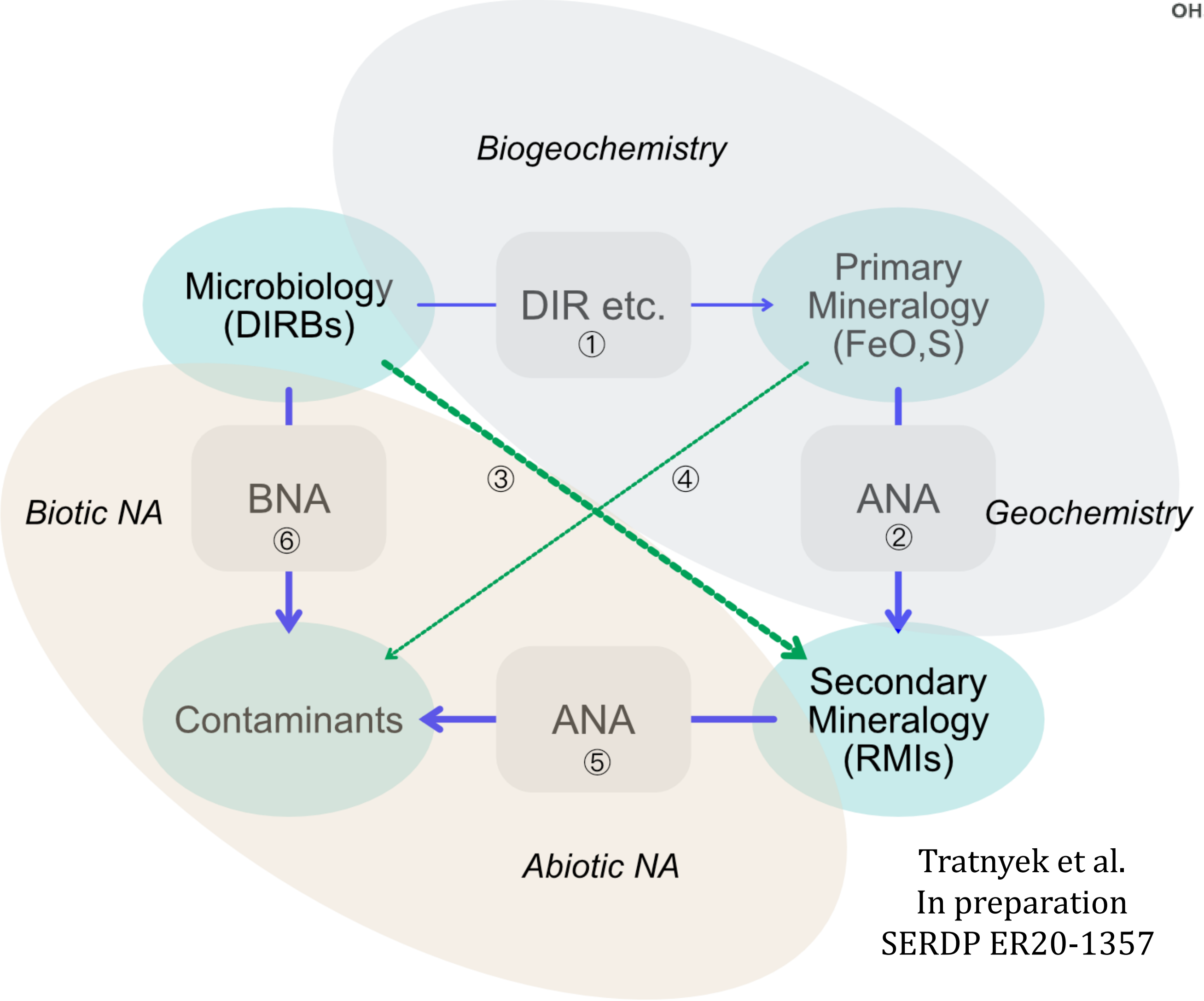
# Biogeochemical Remediation

## Major processes with context

- **Microbiology** (e.g., DIRBs) drives formation of reducing mineral phases directly (①,③) and indirectly (②).
- **Contaminants** can be reduced by Microbes (⑥), **1°Minerals** (④), and/or **2°Minerals** (e.g. RMIs)(⑤).
- **Hypothesis**: ANA of CEs is mostly by RMIs (⑤), not 1°FeO/S (④).
- **Corollaries**: Creating and sustaining RMIs may be altered by Natural Hydrobiogeochemical (**HBGC**) fluctuations or Active-Passive Transitions (**APTs**).

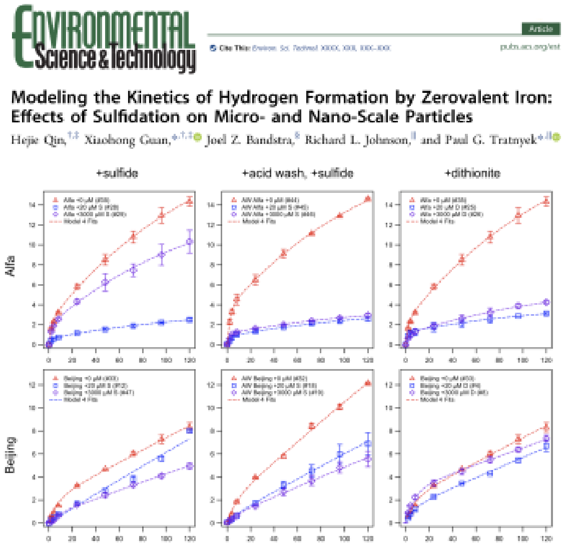


Tratnyek et al.
In preparation
SERDP ER20-1357

# Reactive Mineral (Intermediate) Phases

## Evidence for reactivity

- RMI Hypothesis:
  - *Active precipitation* leads to
  - *Metastable phases* that serve as
  - *Reactive mineral intermediates* (RMIs)
  - Which are the main cause of ANA
- RMI Characteristics:
  - Authigenic (formed in situ); transient when sampled for ex situ analysis
  - Life-time and concentration determined by the balance of source and sink processes.
  - Low steady-state concentration with high turnover can give significant contaminant degradation.

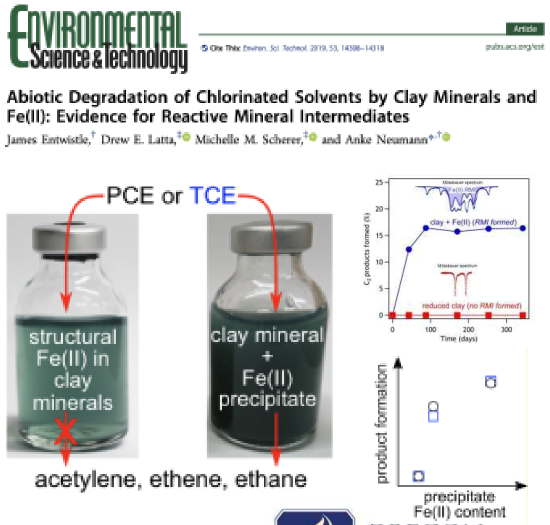


Environmental Science & Technology — Article

Cite This: Environ. Sci. Technol. XXXX, XXX, XXX−XXX — pubs.acs.org/est

**Modeling the Kinetics of Hydrogen Formation by Zerovalent Iron: Effects of Sulfidation on Micro- and Nano-Scale Particles**

Hejie Qin,[†,‡] Xiaohong Guan,[*,†,‡] Joel Z. Bandstra,[§] Richard L. Johnson,[‖] and Paul G. Tratnyek[*,‖]

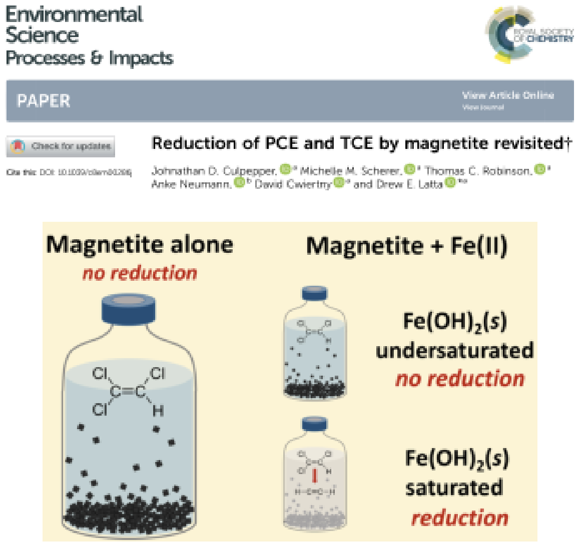


Environmental Science & Technology — Article

Cite This: Environ. Sci. Technol. 2019, 53, 14308−14318 — pubs.acs.org/est

**Abiotic Degradation of Chlorinated Solvents by Clay Minerals and Fe(II): Evidence for Reactive Mineral Intermediates**

James Entwistle,[†] Drew E. Latta,[‡] Michelle M. Scherer,[‡] and Anke Neumann[*,†]



Environmental Science Processes & Impacts

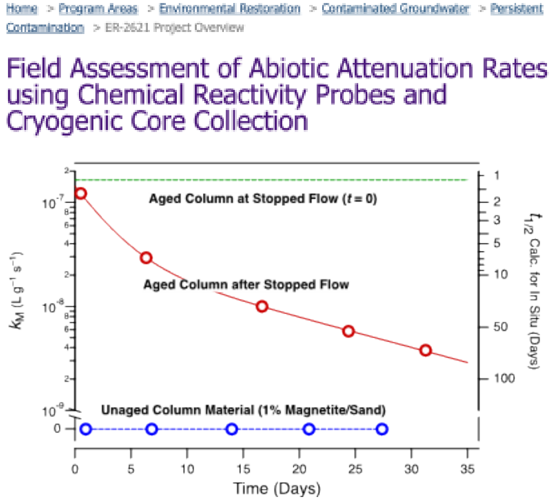
PAPER — View Article Online / View Journal

Check for updates

Cite this: DOI: 10.1039/c8em00286j

**Reduction of PCE and TCE by magnetite revisited†**

Johnathan D. Culpepper,[a] Michelle M. Scherer,[a] Thomas C. Robinson,[a] Anke Neumann,[b] David Cwiertny[a] and Drew E. Latta[*a]



Home > Program Areas > Environmental Restoration > Contaminated Groundwater > Persistent Contamination > ER-2621 Project Overview

**Field Assessment of Abiotic Attenuation Rates using Chemical Reactivity Probes and Cryogenic Core Collection**

# Reactive Mineral (Intermediate) Phases

## Evidence for occurrence and distribution

Paul Tratnyek
tratnyek.org
OHSU

Journal of Hazardous Materials 420 (2021) 126600

Contents lists available at ScienceDirect

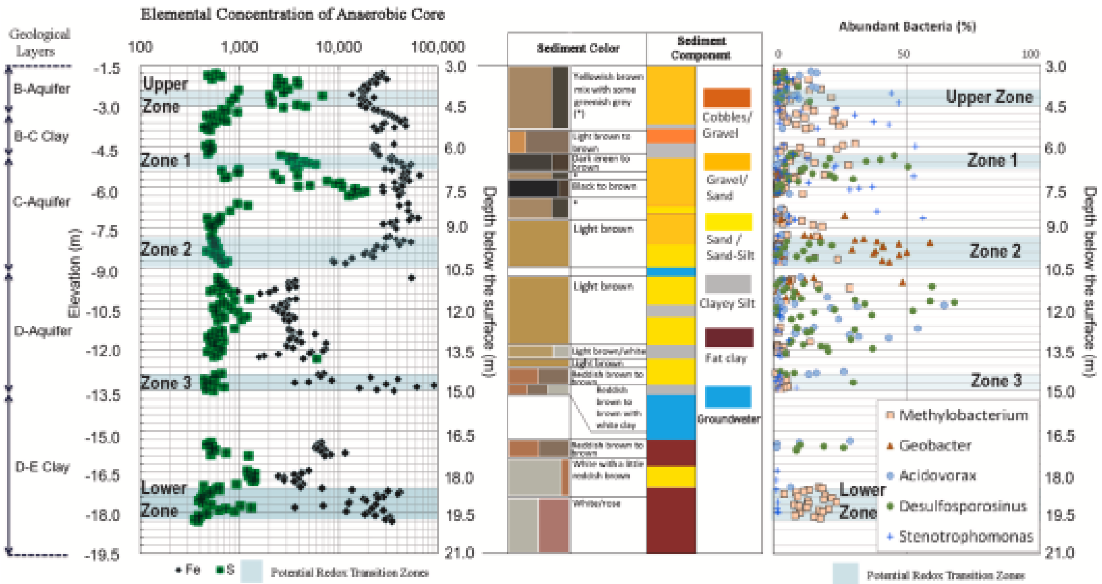
Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

ELSEVIER

Roles of reactive iron mineral coatings in natural attenuation in redox transition zones preserved from a site with historical contamination

Han Hua[a], Xin Yin[a], Donna Fennell[b], James A. Dyer[c], Richard Landis[d], Scott A. Morgan[e], Lisa Axe[f,*]



nature geoscience

2021, 14(5): 264-272

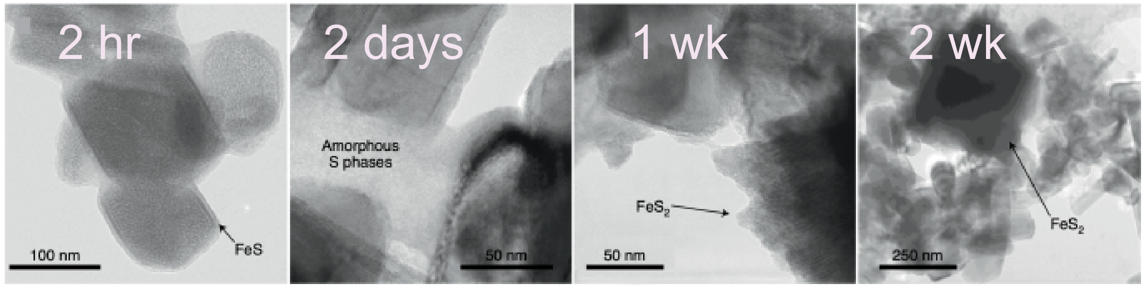
REVIEW ARTICLE

https://doi.org/10.1038/s41561-021-00742-z

Check for updates

A biogeochemical–hydrological framework for the role of redox-active compounds in aquatic systems

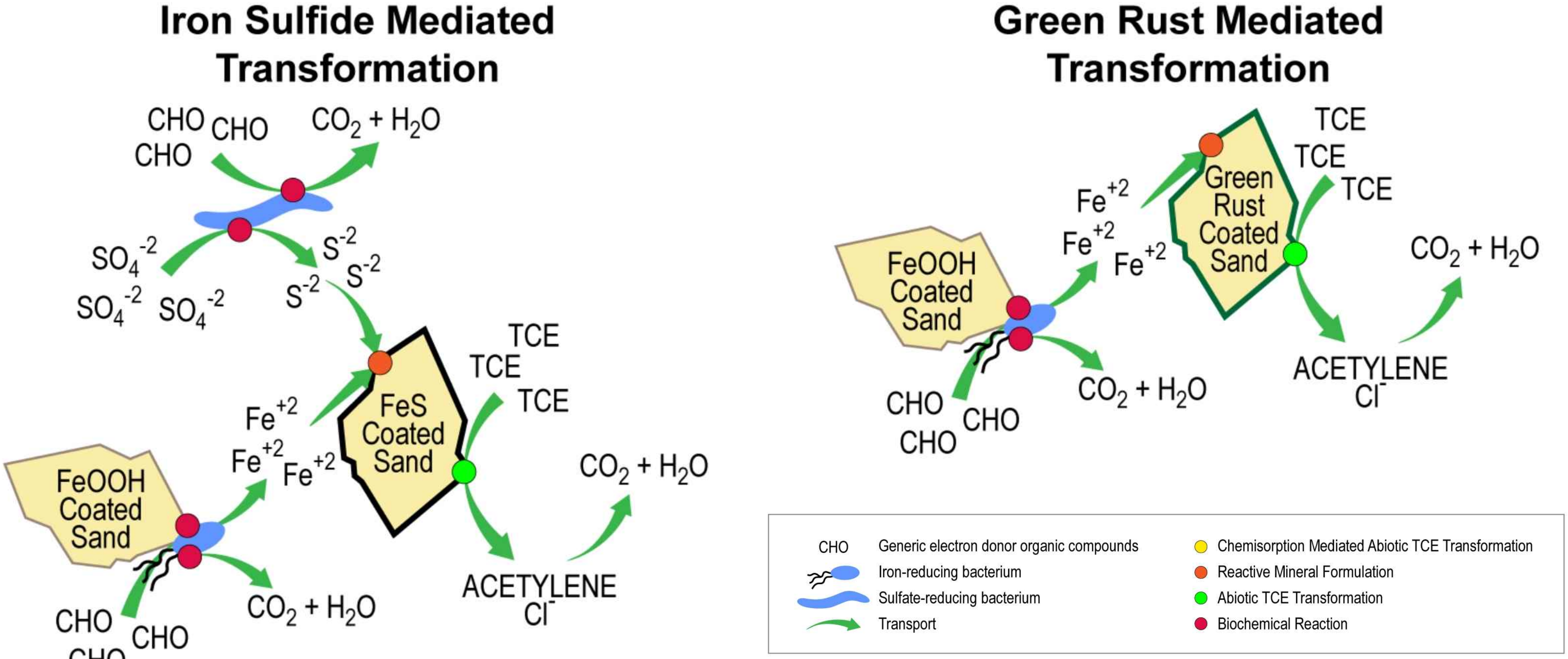
S. Peiffer[1✉], A. Kappler[2], S. B. Haderlein[3], C. Schmidt[2], J. M. Byrne[2], S. Kleindienst[4], C. Vogt[5], H. H. Richnow[5], M. Obst[6], L. T. Angenent[7], C. Bryce[2], C. McCammon[8] and B. Planer-Friedrich[9]



Dynamic processes involving the formation of RAMPs. TEM images showing the reaction between sulfide and lepidocrocite over time.

# Reactive Mineral (Intermediate) Phases

## Mediators of BiRD, ISBGT, BMAD, etc.

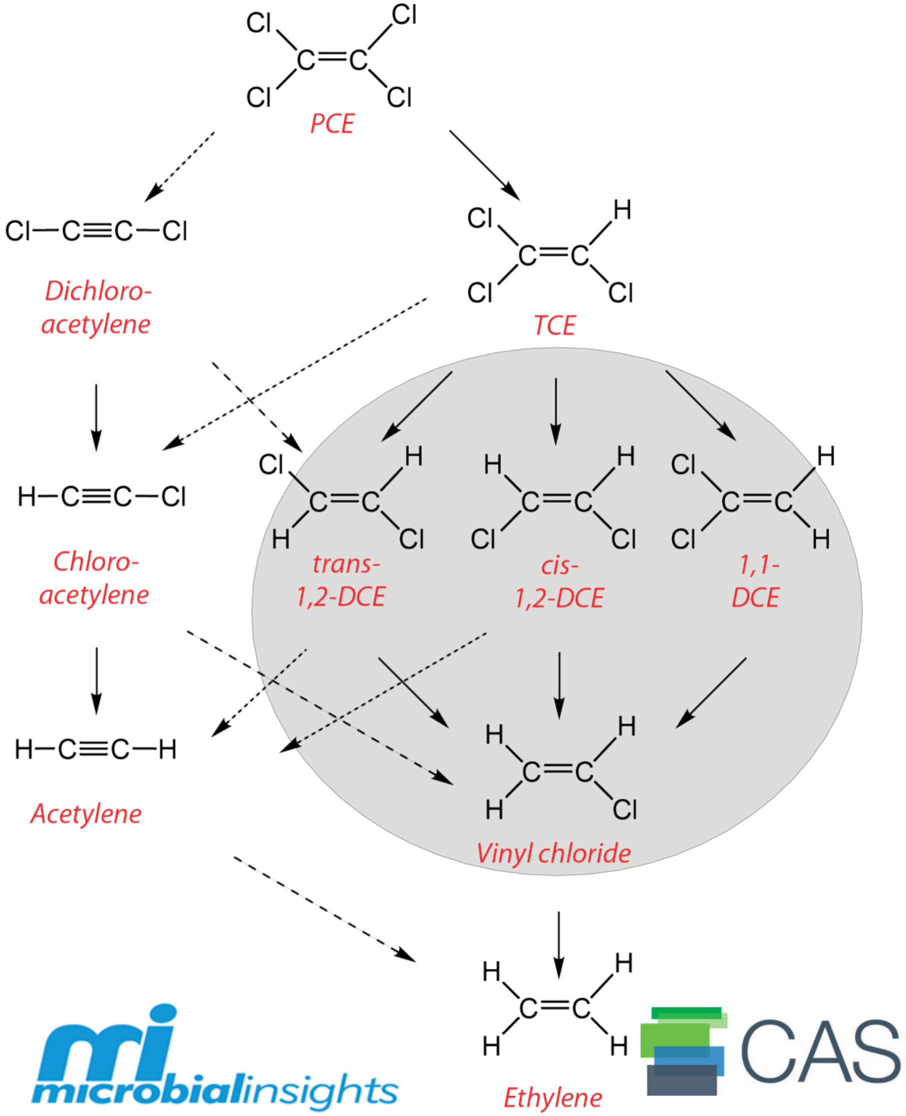

**Iron Sulfide Mediated Transformation**

**Green Rust Mediated Transformation**

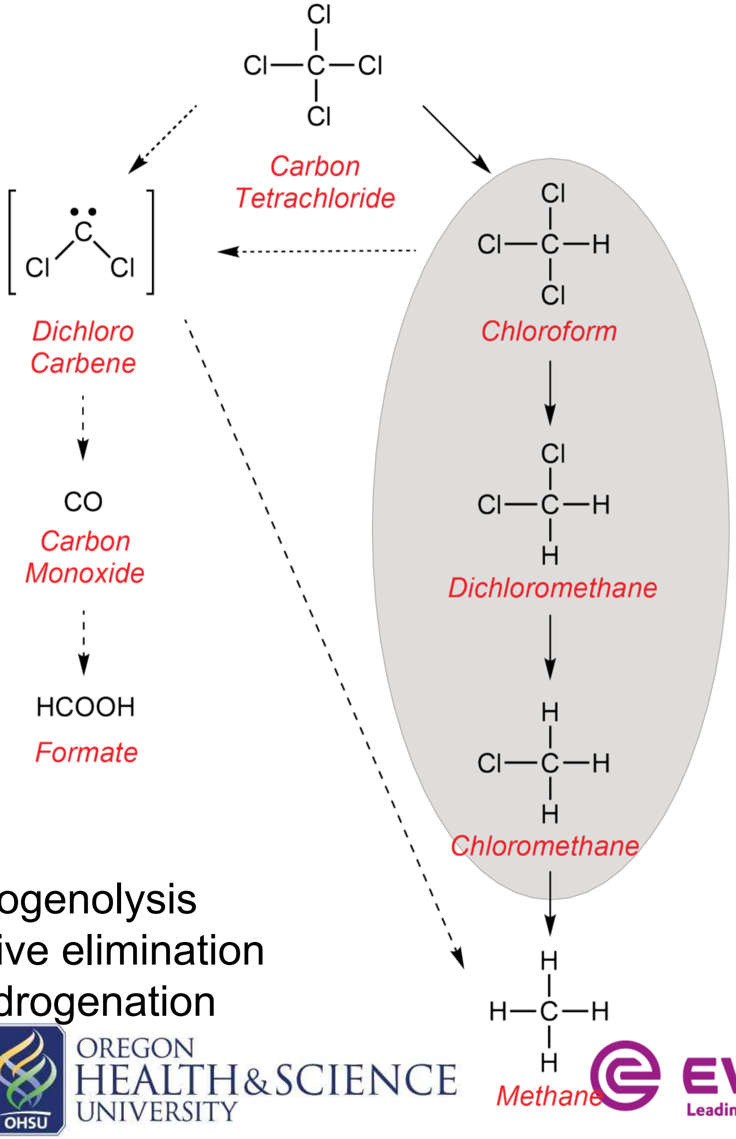
Becvar, Evans, et al. (2008) AFCEE/ESTCP Workshop Report

# Parallel Pathways of Reductive Degradation

## Abiotic vs. biotic pathways



**“Stall” Intermediates in blue ovals**



*Solid arrows*: hydrogenolysis
*Dotted arrows*: reductive elimination
*Dashed arrows*: hydrogenation

Tratnyek, Johnson, Lowry, Brown (2014) SERDP Book Series, v7

# Questions?

# Design Considerations

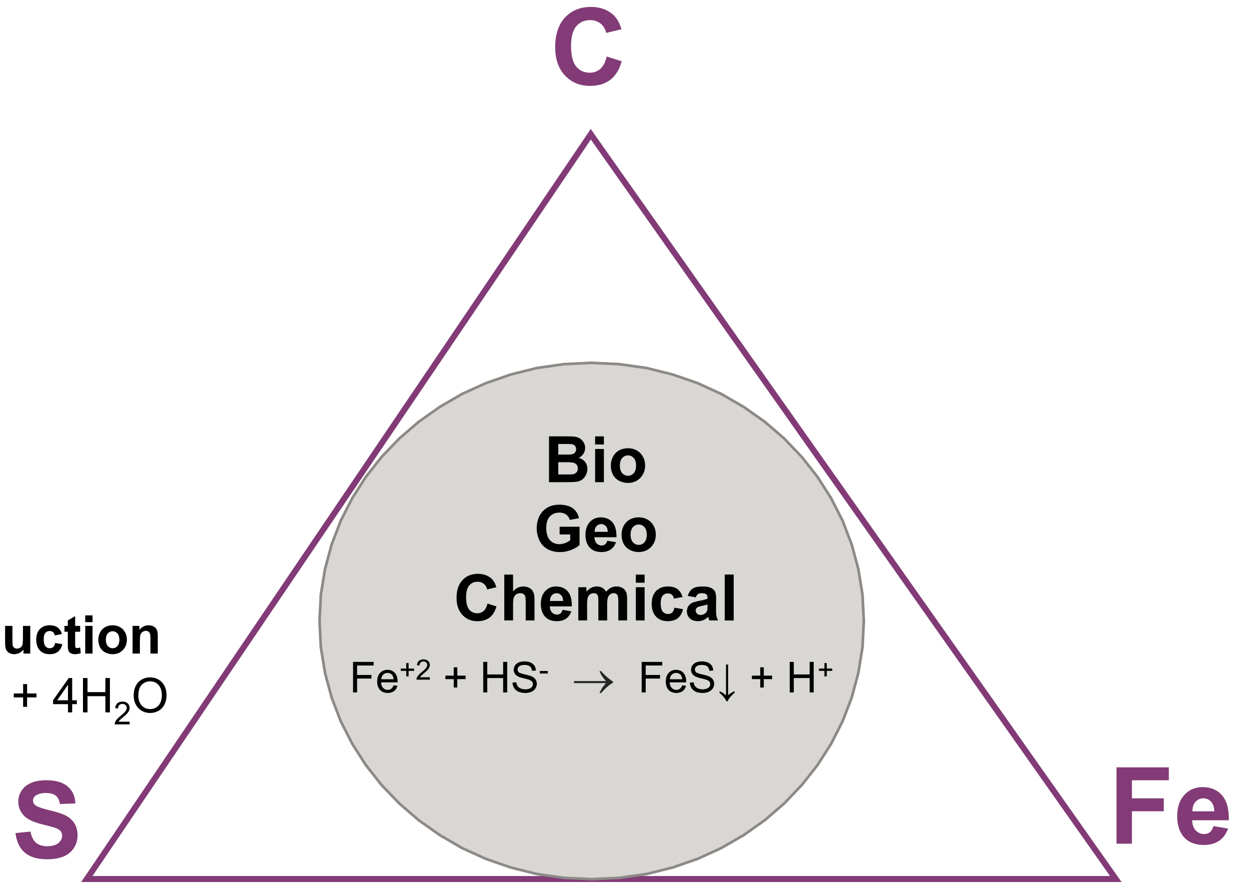
Dr. Alan Seech
Evonik

# Essential Components of Effective BioGeoChemical Remediation

## Adequate availability of all three is Essential (remove limiting parameters)

**Microbial Carbon Metabolism to VFA**

$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$



**Bio Geo Chemical**

$Fe^{+2} + HS^{-} \rightarrow FeS\downarrow + H^{+}$

**Microbial Sulfate Reduction**

$SO_4^{-2} + 9H^{+} + 8e^{-} \rightarrow HS^{-} + 4H_2O$

**Oxidation of ZVI**

$Fe^{0} \rightarrow Fe^{+2} + 2e^{-}$

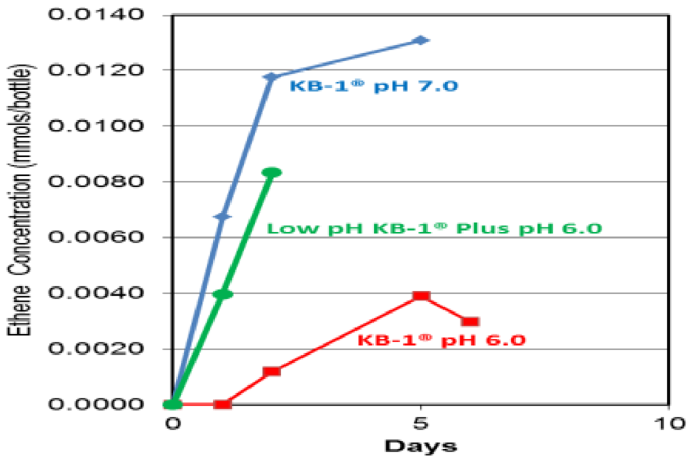
$2H_2O \rightarrow 2H^{+} + 2OH^{-}$

$2H^{+} + 2e^{-} \rightarrow H_{2\,(g)}$

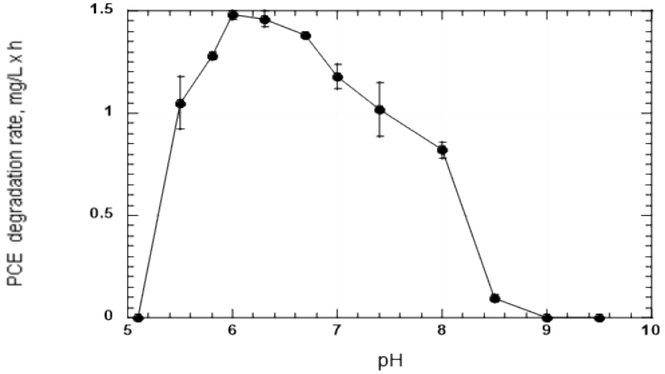
# Target Conditions Generate BioGeoChemical Remediation Zone

## TOC, Sulfate, and Dissolved Iron from Aquifer and Reagents

- ✓ **pH between 6.0 and 7.5**
  - Outside this range DHC activity is inhibited
  - pH at the lower end of this range helps to keep iron in solution
  - ZVI passivation increases at higher pH as siderite↓ increases
  - Above pH of 7.5 microbial sulfate reduction is sharply inhibited
- ✓ **ORP below -200 mV**
  - Helps to keep $Fe^{+2}$ in solution
  - Sulfate reduction requires ORP below 150 mV
  - Thermodynamics of dechlorination are better at lower ORP
- ✓ **TOC between 1,000 and 3,000 mg/L**
  - Adequate electron donor to support removal of $O_2$, $NO_3^-$, and $SO_4^{-2}$
  - Produce enough VFA acidity to balance ZVI alkalinity and promote release of $Fe^{+2}$
- ✓ **Sulfate between 500 and 2,000 mg/L**
- ✓ **Dissolved iron of at least 100 mg/L**
  - Availability of $Fe^{+2}$ is probably the rate limiting parameter
  - Need enough to prevent sulfide toxicity by removing sulfide as FeS↓



[redacted]



Effect of pH on PCE degradation rate by SDC-9 consortium.

*Figures provided by P. Dennis, SiRem (top) and S. Vainberg, APTIM (bottom)*

| Process | Results & Products | Impact on Aquifer pH | Impact on Aquifer ORP | Impact on ZVI | Impact on Reactive Minerals |
|---|---|---|---|---|---|
| Microbial Metabolism of Organic Carbon | ▪ removes $O_2$, $NO_3^-$ and $SO_4^{-2}$<br>▪ produces VFAs that promote acidification | ↓ | ↓ | ▪ VFAs ↑ corrosion<br>▪ ↑ $Fe^{+2}$ release<br>▪ ↓ passivation | ▪ ↑ solubility of FeS and $FeS_2$ |
| Microbial Sulfate Reduction | ▪ produces $S^{-2}$, $HS^-$ | ↑ (small) | ↓ | ▪ ↑ ZVI corrosion<br>▪ ↑ $Fe^{+2}$ release<br>▪ ↑ in situ sulfidation | ▪ ↑ rate & extent of FeS formation<br>▪ ↑reactivity of FeS |
| Oxidation of ZVI (corrosion) | ▪ produces $Fe^{+2}$, $e^-$<br>▪ produces $OH^-$ | ↑ | ↓ | ▪ ↑ passivation in high $O_2$ or $HCO_3^-$ environments | ▪ ↑ rate & extent of FeS formation<br>▪ ferruginous clay |

# Carbon Metabolism, Microbial Sulfate Reduction, and Iron Corrosion

## Important Interactions

Microbiologically enhanced corrosion of iron by sulfate reducing bacteria during growth on cellulose.

*K.H. Logan In: The Corrosion Handbook. H.H. Uhlig (Ed). 1946. John Wiley & Sons, NY.*

- Cast iron pipe in wet soil
- Wrapped in cellulose (hemp) rope
- Long-lasting source of organic carbon to support removal of $O_2$, and $NO_3^-$ which promotes onset of $SO_4^{-2}$ reduction
- Enhanced corrosion and release of $Fe^{+2}$
- Sulfate reducing bacteria isolated from pitted areas produce $HS^-$
- $HS^-$ combines with $Fe^{+2}$ to form FeS precipitate
- Stronger negative Eh in the pitted areas
- Adequate supply of $Fe^{+2}$ prevents high concentration of free sulfide which can inhibit continued sulfate reduction

# Sulfidation increases ZVI reactivity and Longevity

**“Sulfidation” … can refer to any modification or transformation of a metal-based material by exposure to sulfur compounds of various oxidation states…”**

## In Situ Sulfidation Process:

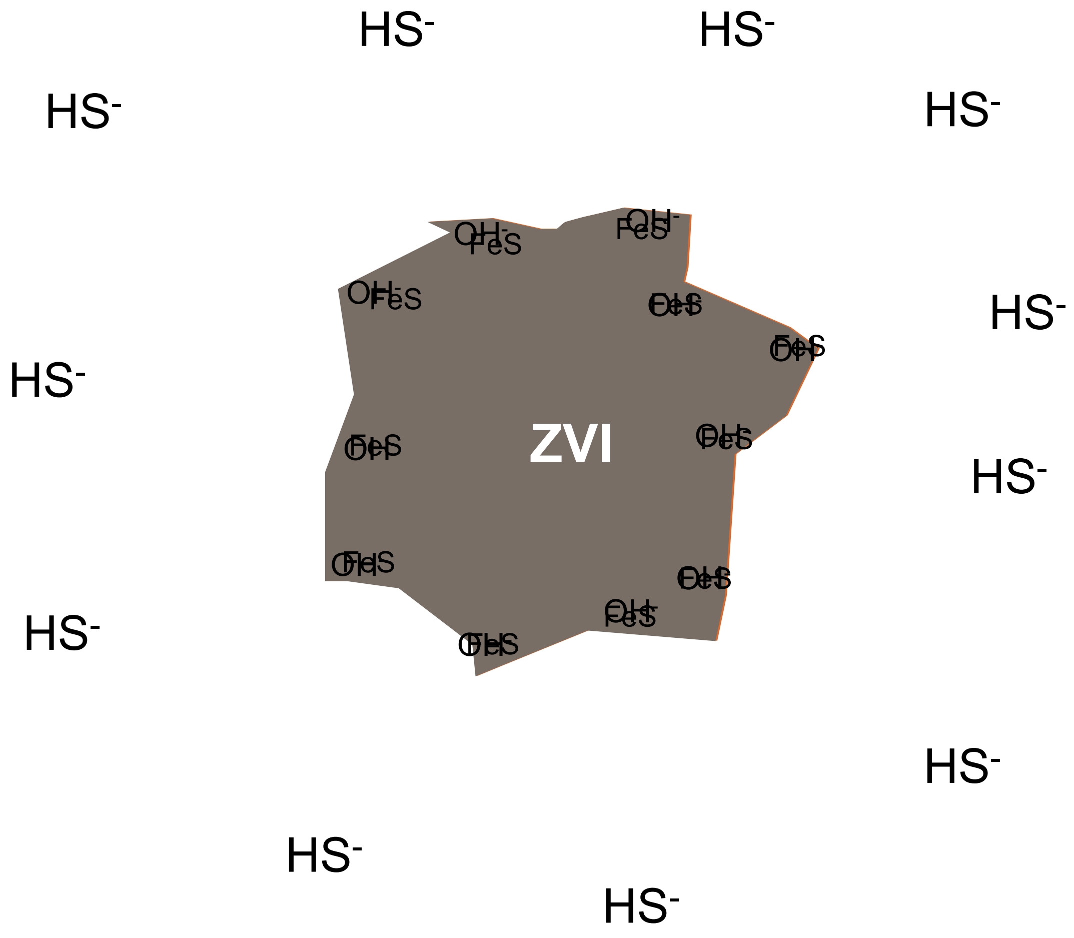
ZVI, $Fe^{+2}$, $SO_4^{-2}$, and organic carbon (**OC**) are distributed in aquifer

ZVI reacts with water to generate $OH^-$ on surface

Sulfate is biologically reduced to sulfide ($HS^-$)

Sulfide replaces $OH^-$ on ZVI particle surface

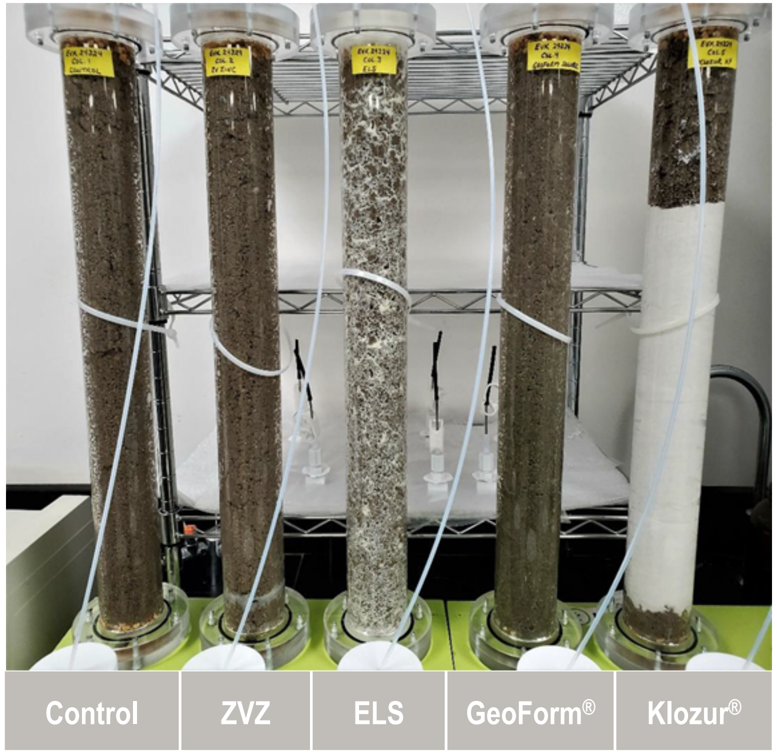
$Fe^{2+}$ (ambient, supplied or from ZVI oxidation,) combines with $HS^-$ to form FeS coating on ZVI



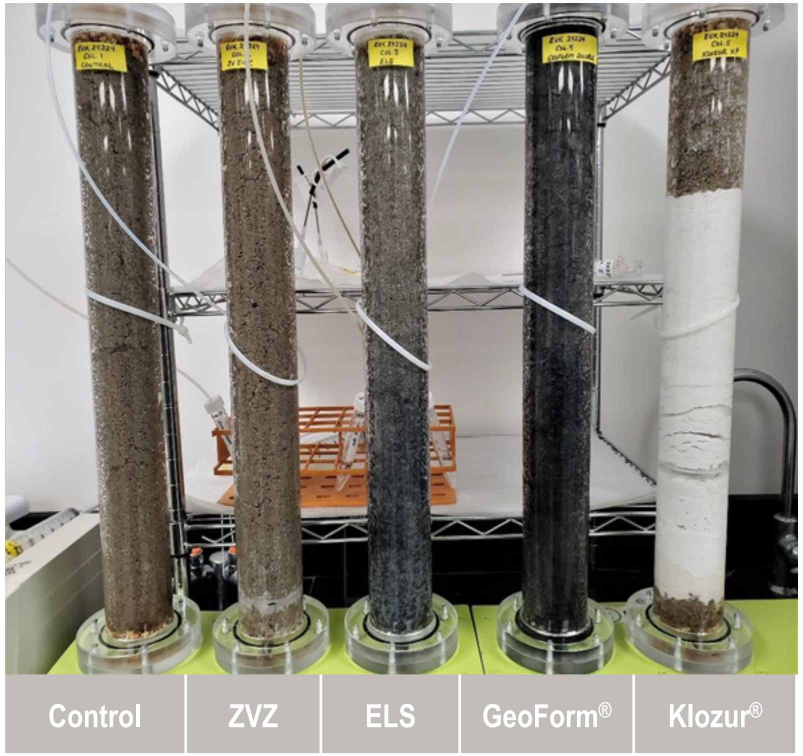
**Sulfidation of Iron-Based Materials: A Review of Processes and Implications for Water Treatment and Remediation. 2017.**
Dimin Fan, Ying Lan, Paul G.Tratnyek, Richard L. Johnson, Jan Filip, Denis M. O’Carroll, Ariel Nunez Garcia, and Abinash Agrawal, Environmental Science & Technology.

# Visual Evidence for Establishment of Effective BioGeoChemical Conditions

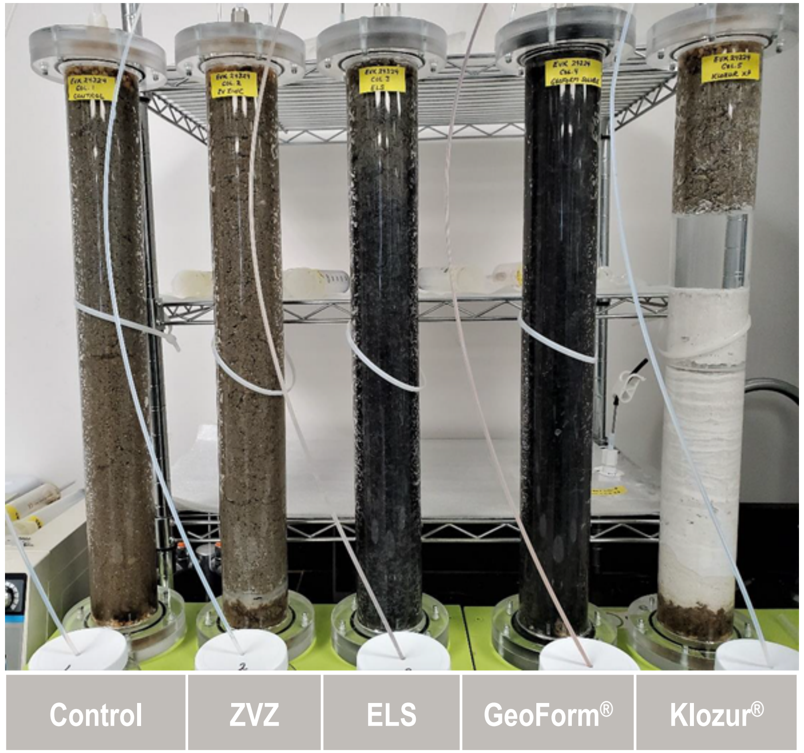
## Day 1



## Day 56



## Day 130



### Day 56 Monitoring

| Parameter | Influent | Control | ZVZ | ELS® | GeoForm® S | Klozur® SP |
|---|---|---|---|---|---|---|
| Eh (mV) | 367 | 212 | 200 | -131 | -139 | 226 |
| pH (s.u.) | 7.4 | 7.6 | 7.7 | 6.6 | 7.0 | 12.7 |

# Questions?

[

# Injection and Fracturing Considerations for Bio-Geochemical Liquid and Solid Amendments

Eric Moskal, Cascade Remediation Services

emoskal@cascade-env.com

CASCADE

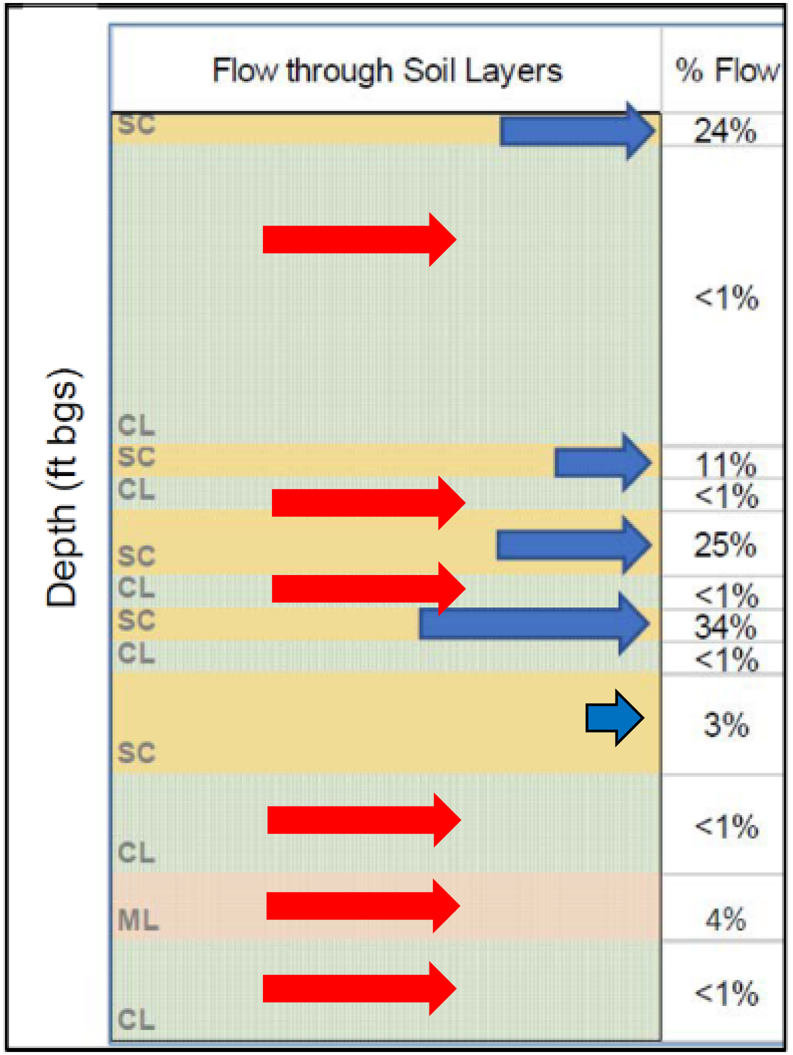
# Site Design Strategy From an Injection Implementation Standpoint

- Understanding site geology is crucial to defining remediation approach
  - High-resolution site characterization (HRSC) used to build detailed CSM

- Geology dictates amendment state
  - Suspended Solids (ZVI, EHC, Geoform ER, etc.)
  - Dissolved or colloidal (Colloidal ZVI, EHC-Liquid, Geoform Soluble, etc.)

- Geology and selected amendments dictate emplacement methodology
  - Low pressure/low flow for pore volume replacement
  - High pressure/high flow for fracturing and solids emplacement

# What Do You Treat… Transmissive and/or Storage Zones?



90% of GW flows through 30% of cross-sectional area

Injection

- Liquids
- Colloidal Solids

This includes filling these zones as well as "painting" the interfaces with long-lasting amendments to manage the slow flux coming off finer grained matrix back diffusion.

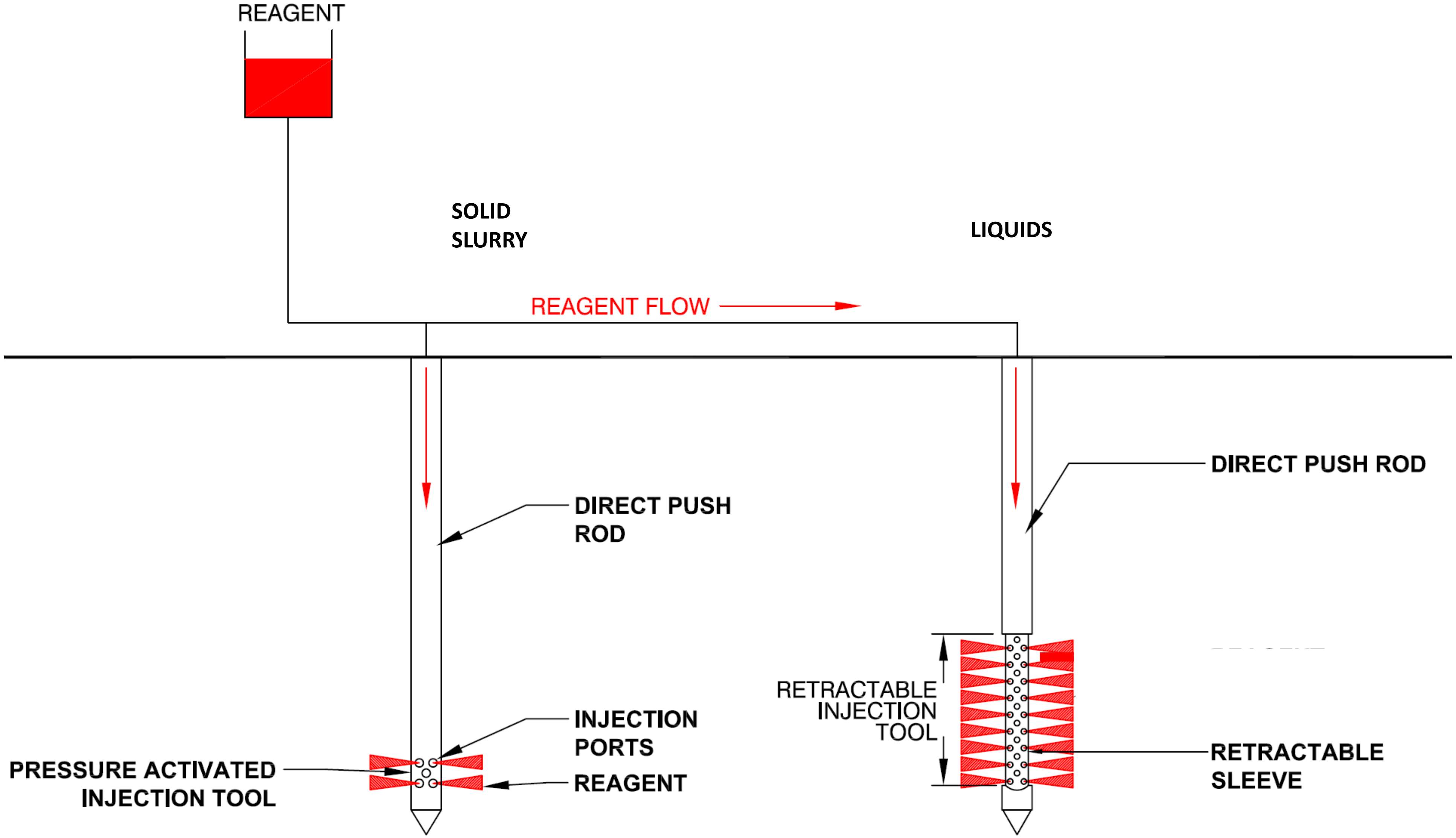
10% of GW flows through 70% of cross-sectional area

Fracturing

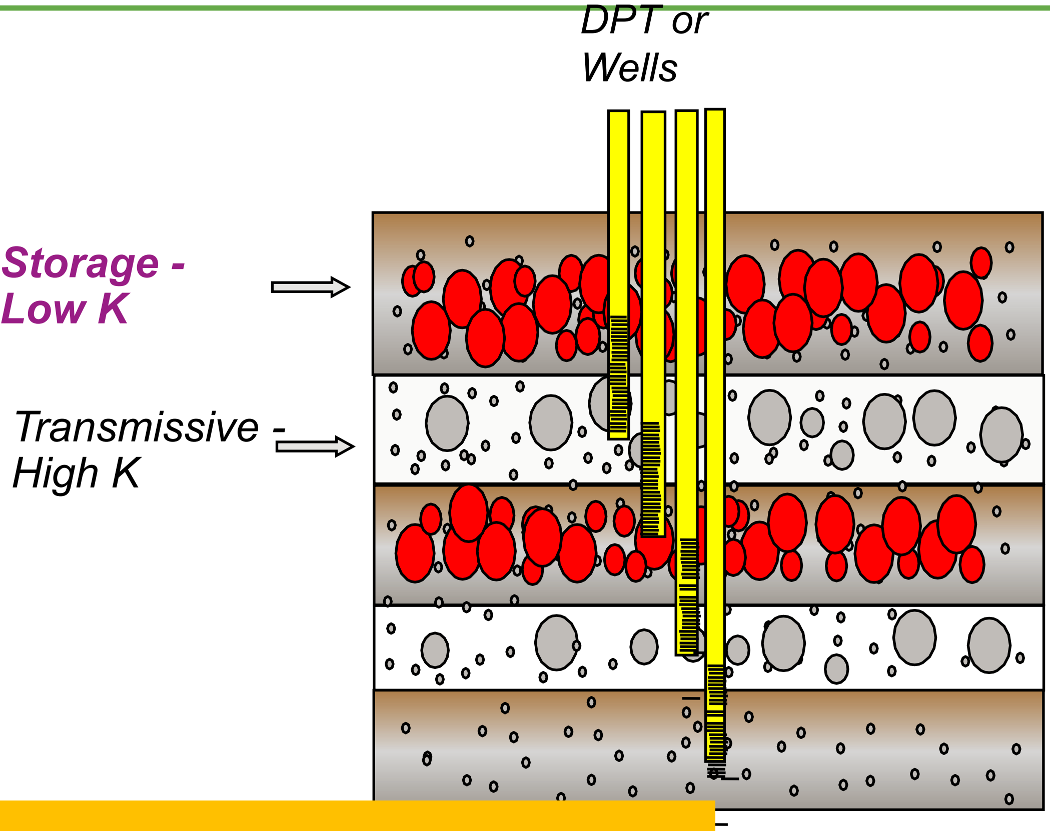
- Solids

Fracturing and permeability enhancement have been proven to be effective when applied to media such as silt, clay, weathered rock

# DPT Direct Push Liquid and Solid Tooling



# Transmissive (High K) Strategy: Liquids with Traditional or Automated Injection



*Transmissive -High K – Overlap Low K and Target Through Pressure Control*

# Evolution of Injection For Liquid Amendments

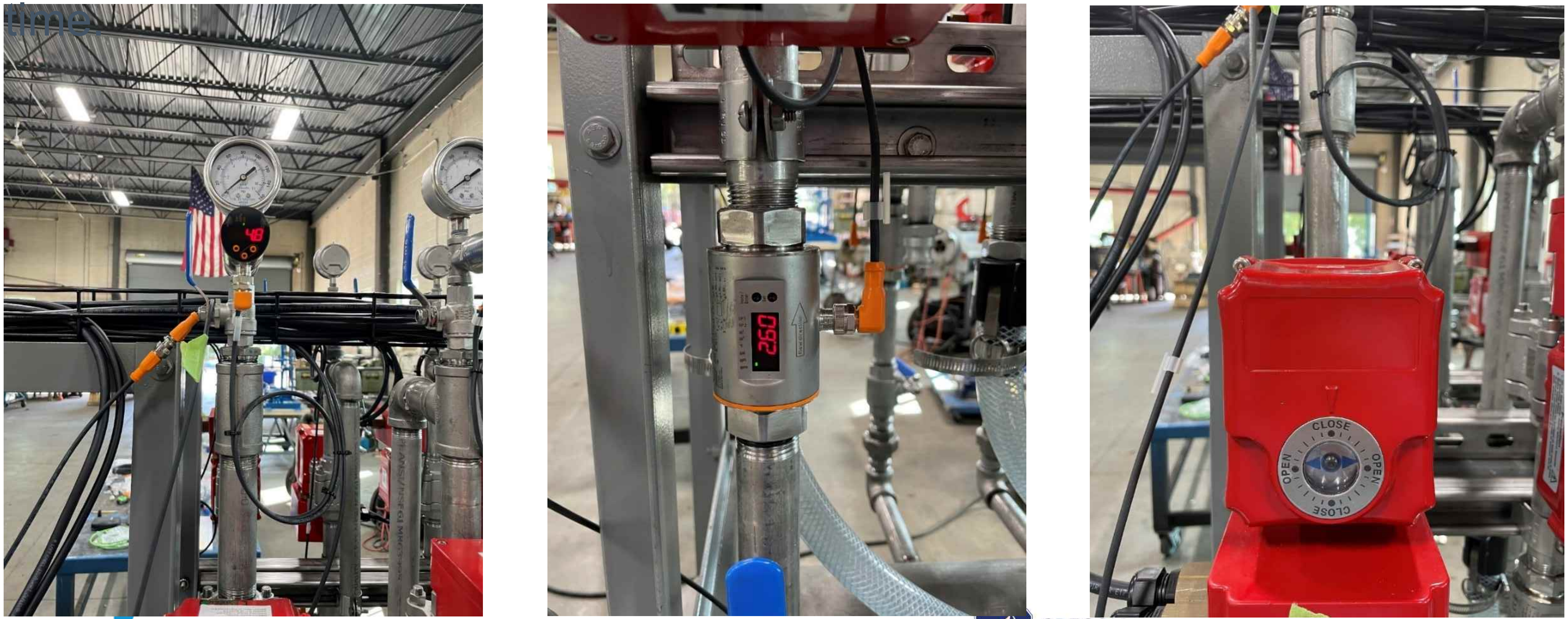
- Few developments of injection technology since its inception in the mid-1990’s beyond…
  - Ball valves
  - Manually read flow meters and pressure gauges
- Sensitivity to injection pressures and flows by our professional community and subcontractors

# DPT Inner-Hose and Screen Tooling




# What Is  Automated Injection?

Automatic control of ball valves from digital pressure and flow readings in real-time.



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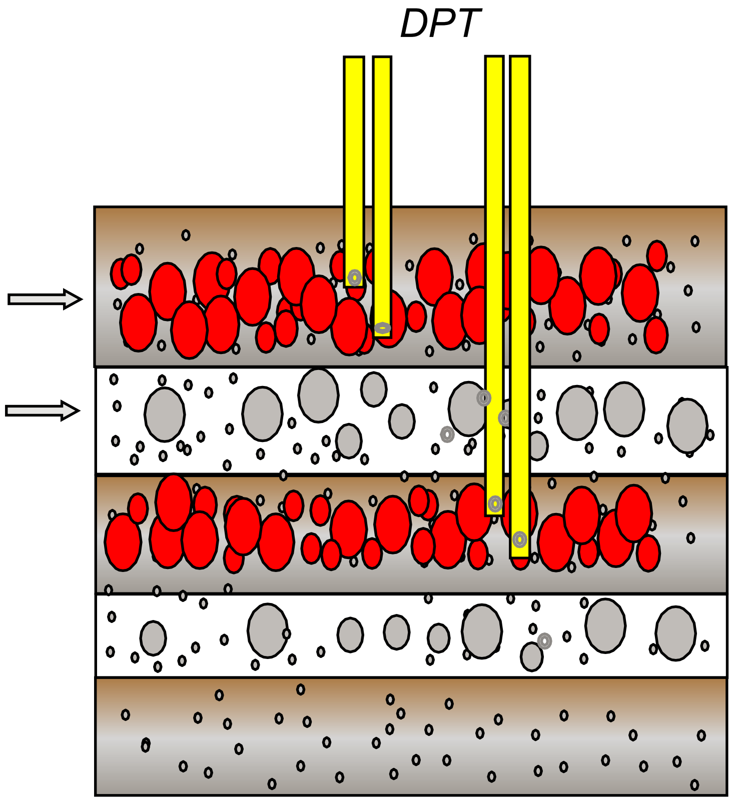
# Storage (Low K) Strategy: Solids Through Hydraulic Fracturing

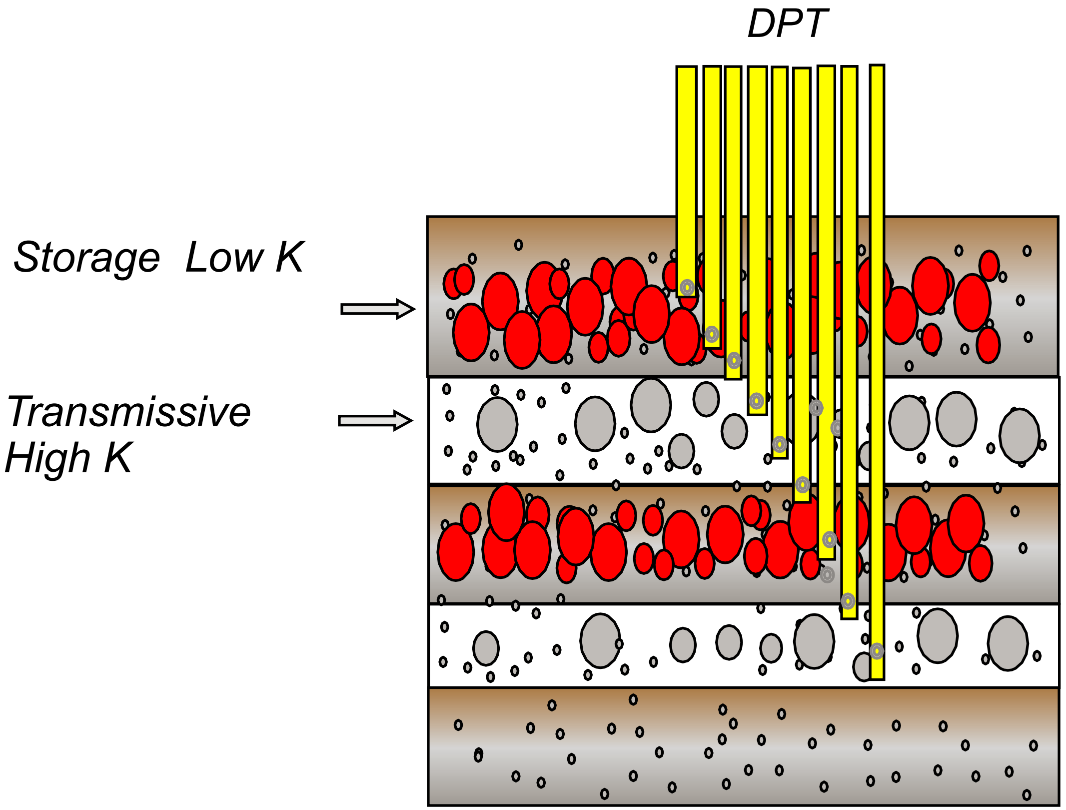
*Storage Low K*

*Transmissive*
*High K*



*Target with Higher Pressure Activated Discreet Tooling.*

# Transmissive (High K) and Storage (Low K) Strategy: Liquids/Solids



*Target with Higher Pressure Activated Discreet Tooling.*

# Storage (Low K) Strategy: Solids Through Pneumatic Fracturing

1. Initiate Fractures With High Pressure Nitrogen.
2. Switch to Hydraulic Injection of Amendments into Fractures.
3. Implemented through Straddle Packers in Open Boreholes, through Sonic Casing, and DPT.
4. Creates new fractures in overburden.
5. Enhances existing fractures in bedrock.

# Thank You!

Eric Moskal

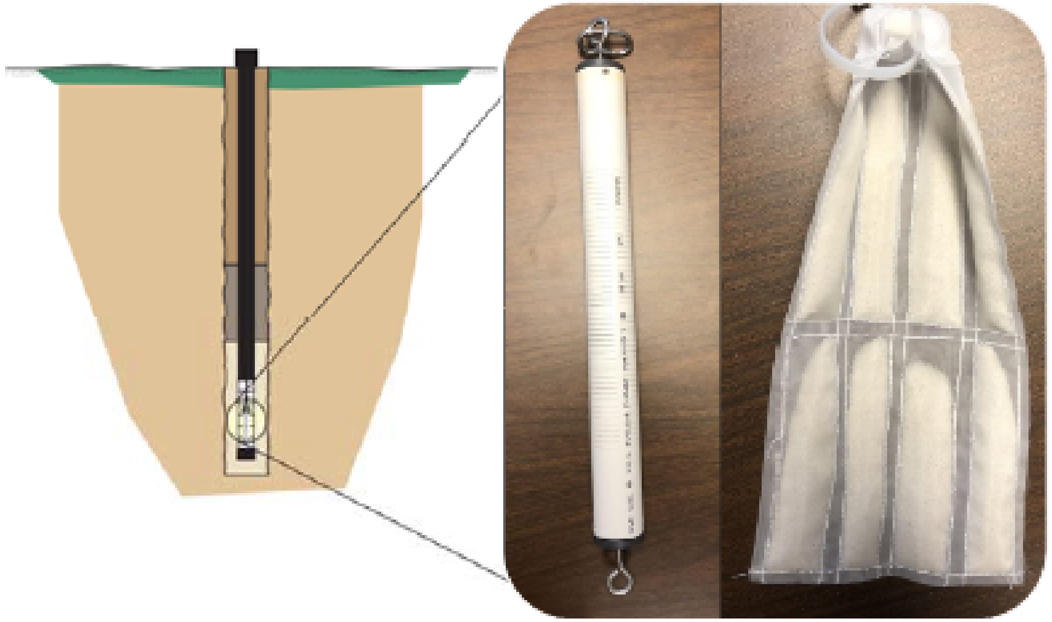
Cascade Remediation Services

emoskal@cascade-env.com

# Monitoring for Biogeochemistries

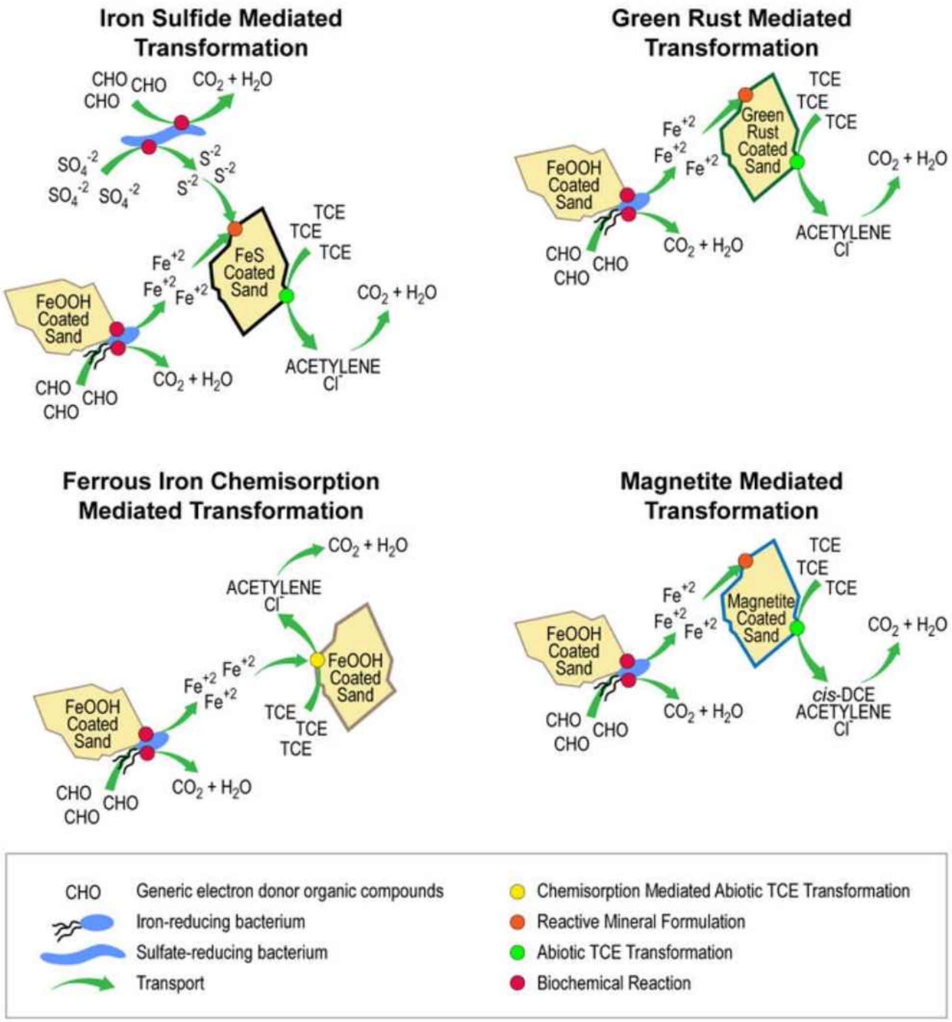
Dora Taggert
Microbial Insights

Min-Trap®



# Groundwater Chemistry

## Monitoring to assess the status of subsurface biogeochemical processes



## Environmental parameters

--factors affecting biological activity and geochemistry

- Electrical Conductivity (EC)
- pH
- Total Dissolved Solids (TDS)
- Temperature
- Alkalinity

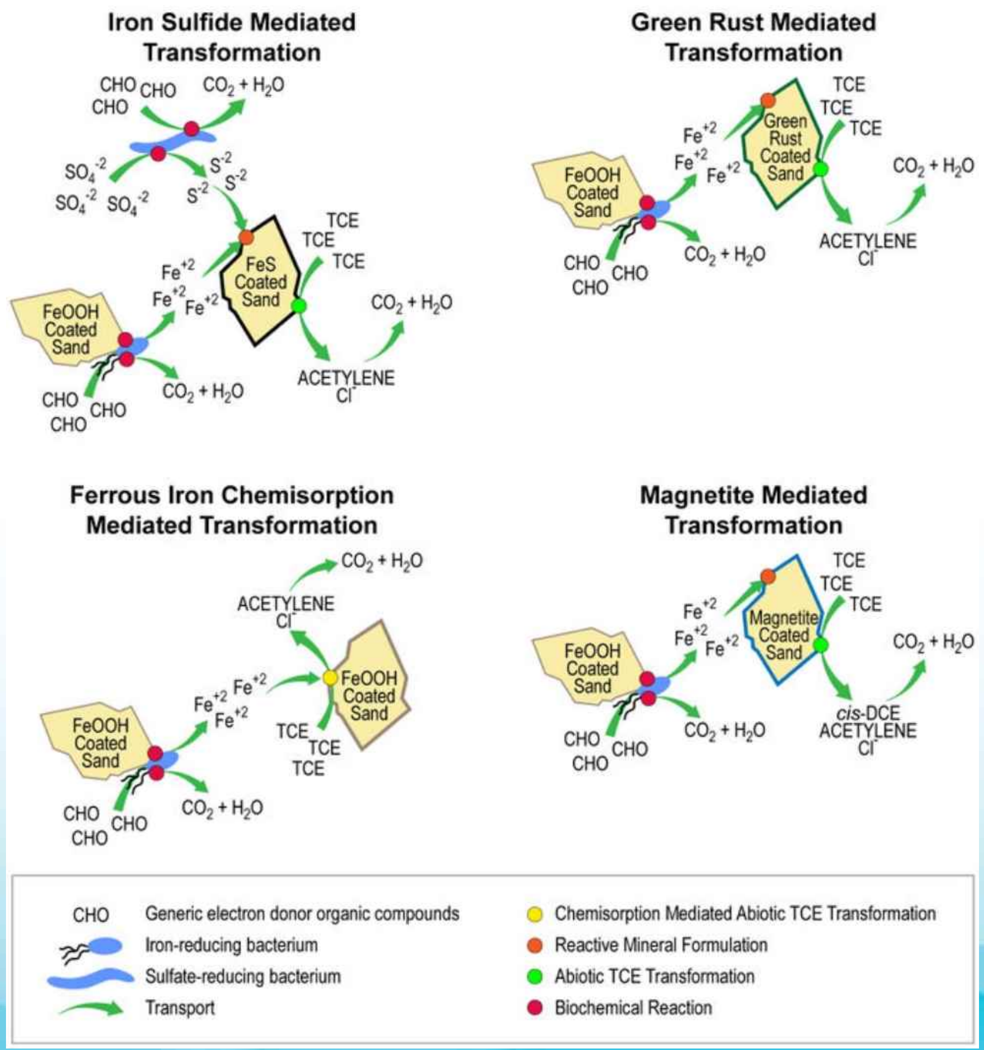
## Electron donors

--potential for sustained biological reduction

- Total Organic Carbon (TOC)
- Volatile Fatty Acids (VFAs)

# Groundwater Chemistry

## Monitoring to assess the status of subsurface biogeochemical processes



### Redox sensitive parameters

---indicators of dominant terminal electron accepting processes

- DO
- ORP
- $Fe^{+2}$
- $SO_4^{-2}$
- $NO_3^-$
- Dissolved methane
- Dissolved hydrogen
- Sulfide, bisulfide

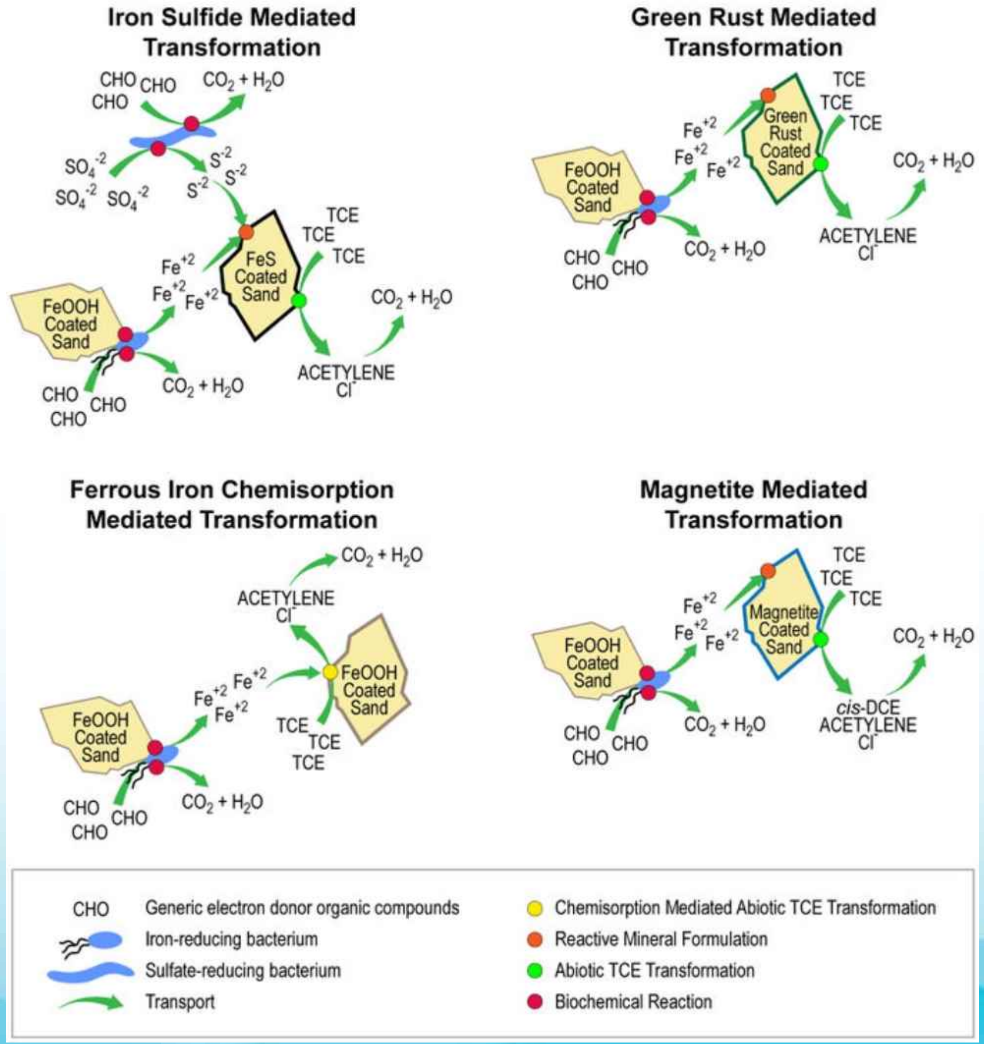
### Contaminants and biodegradation products

---biotic vs. abiotic transformations

- Daughter products
- Ethene, ethane, acetylene
- CSIA

# Sediment Geochemistry

## Monitoring to assess the status of subsurface biogeochemical processes

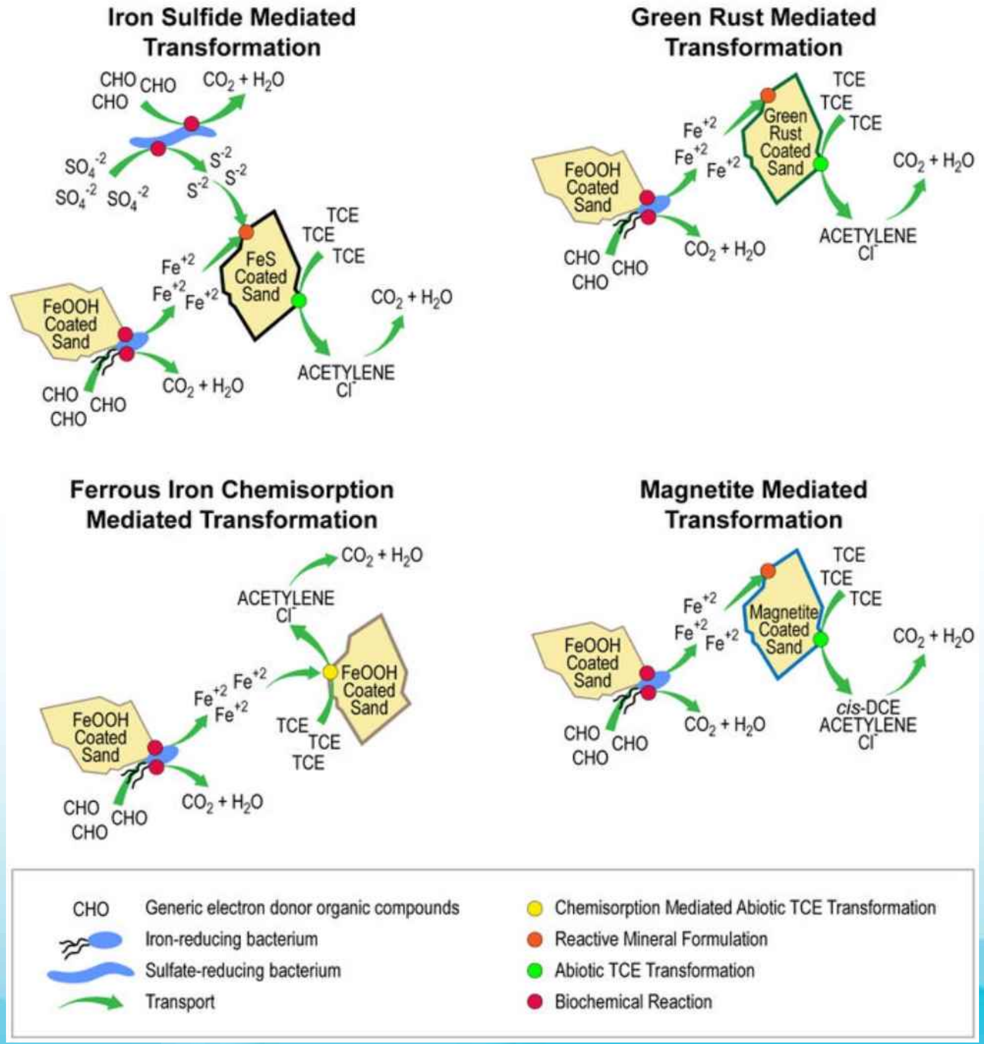


Indicators of active mineral species

- Acid volatile sulfides
- Magnetic susceptibility
- Bioavailable iron
- Humic acids (electron shuttles)
- Specific surface area
- Total Organic Carbon (TOC)
- Iron mineral speciation
  - SEM
  - X-ray diffraction

# Sediment Geochemistry

## Monitoring to assess the status of subsurface biogeochemical processes



## Challenges

Minerals involved in biogeochemical transformations are labile

- Standards for sampling and preservation of anaerobic conditions not well established

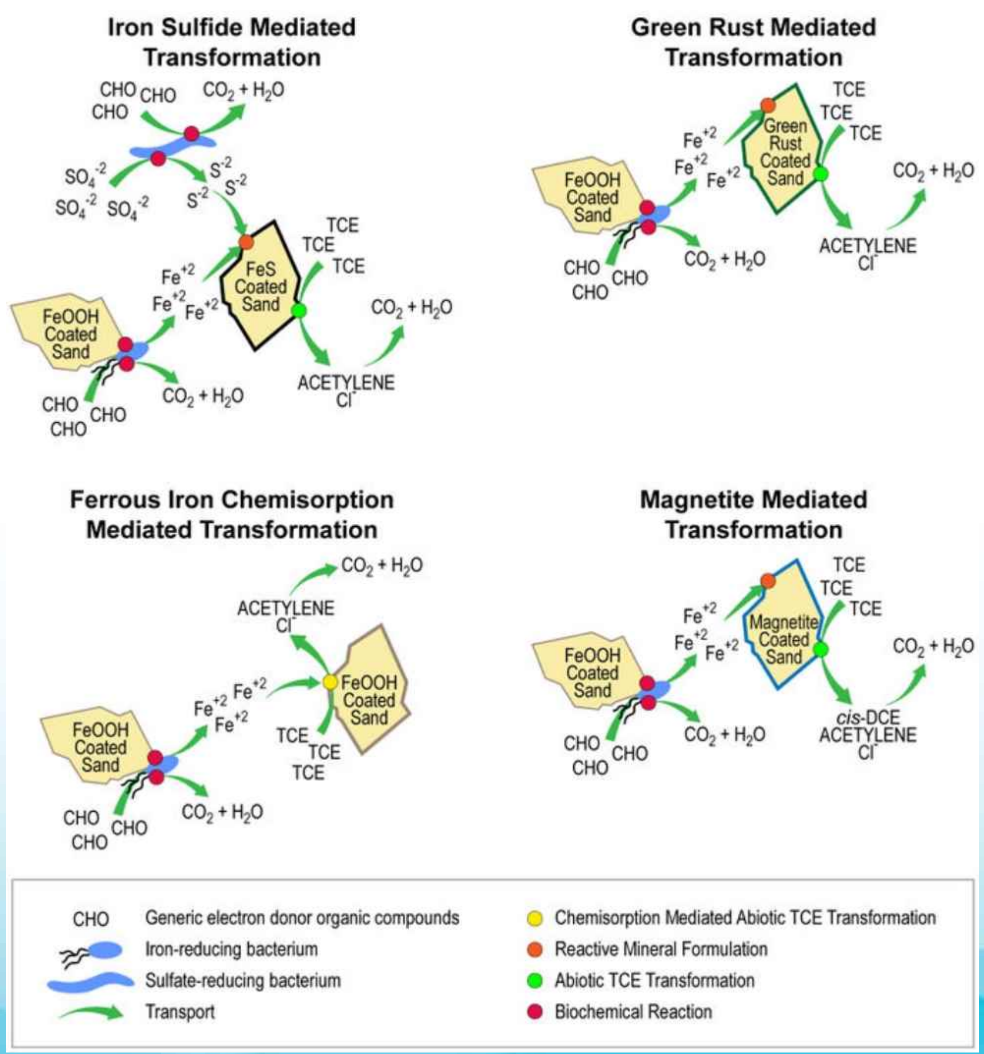
## Site heterogeneity

Where do you core to get representative samples?

Multiple processes ongoing tha are likely spatially separated

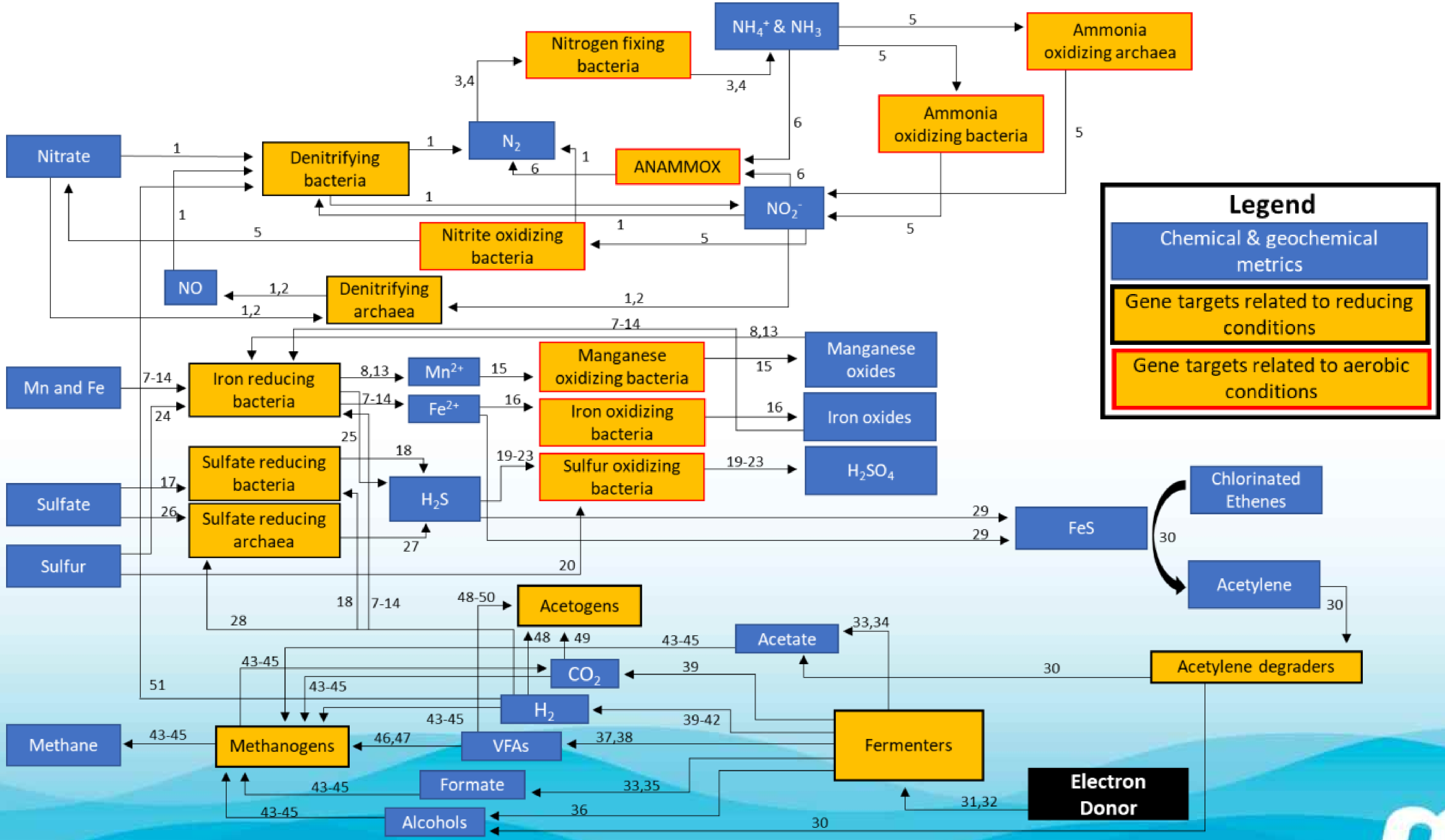
# Microbiology

## Monitoring the bacterial populations of groundwater or sediments

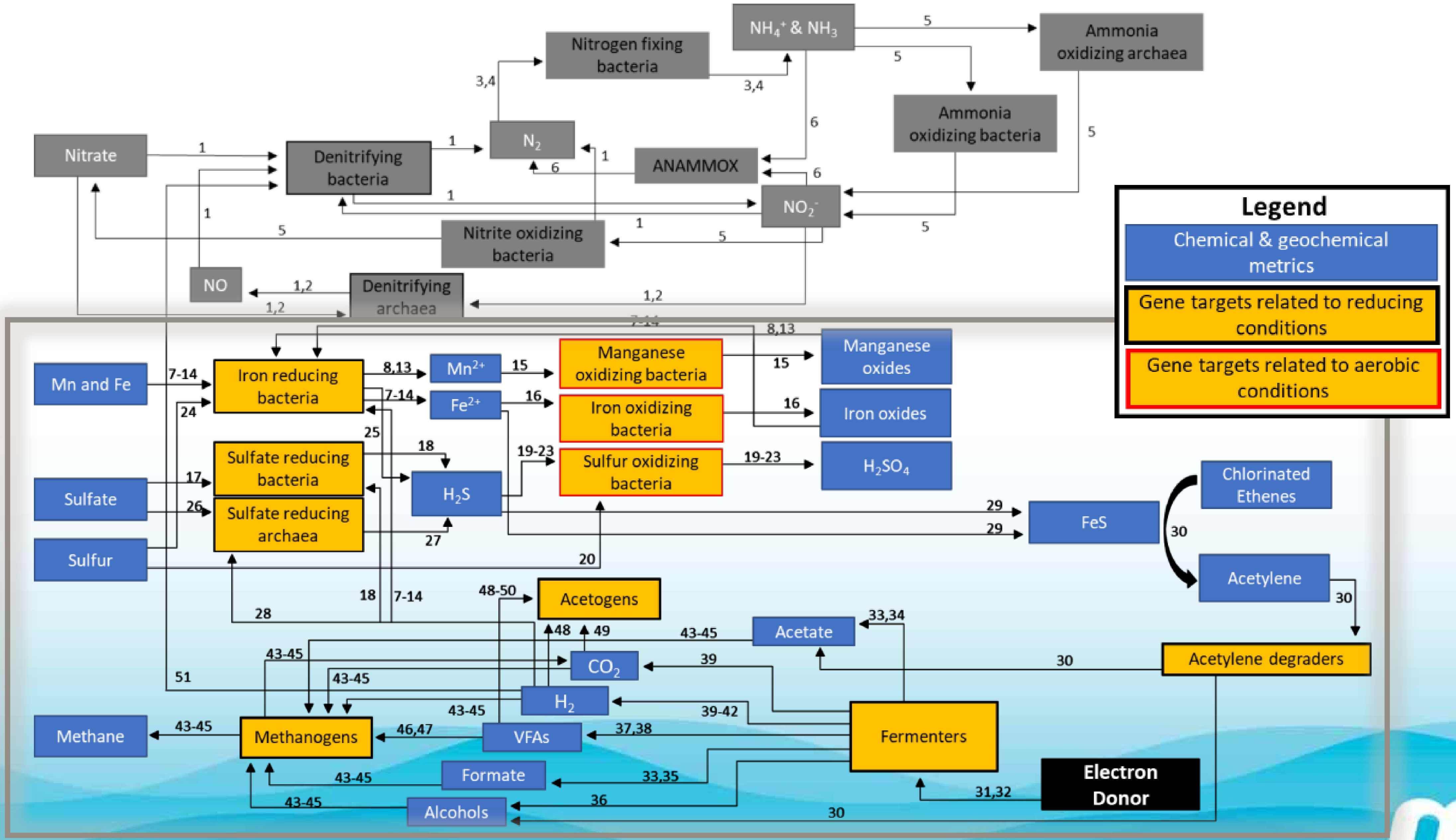


| | |
|---|---|
| General bacterial analysis and temporal changes over time | PLFA |
| Detection and quantification of key genera, species, or functional genes | qPCR |
| Diversity and abundance of bacterial groups | Next Generation Sequencing (NGS) |

# QuantArray-BGC gene targets

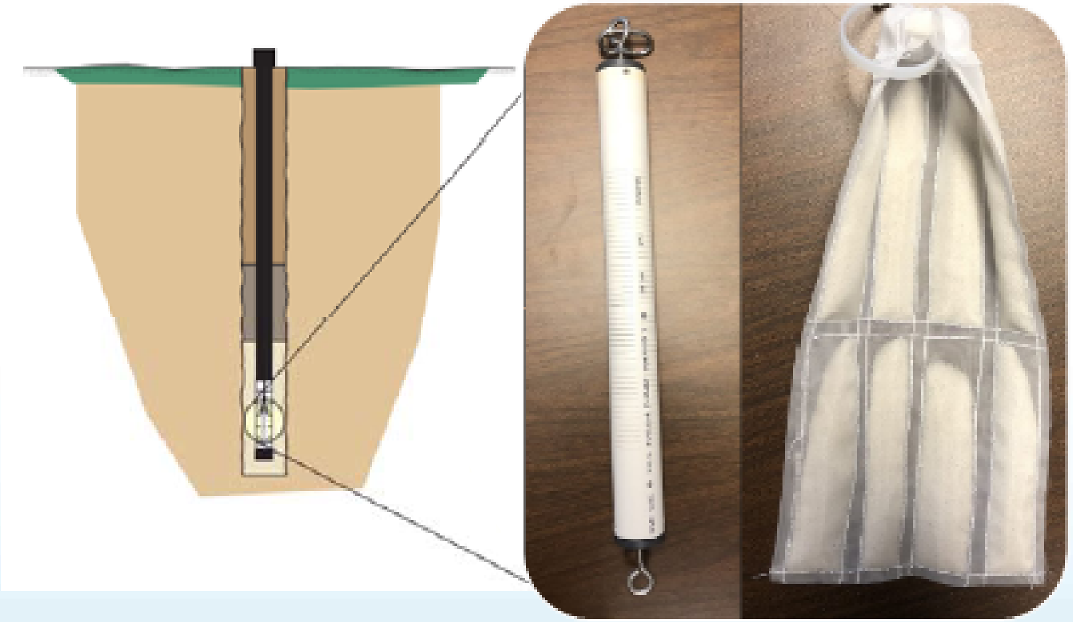


# QuantArray-BGC gene targets



# Min-Trap®

Min-Trap®



# Questions?

[

# Biogeochemically Enhanced Treatment of Chlorinated Organics and Metals
## Case Studies

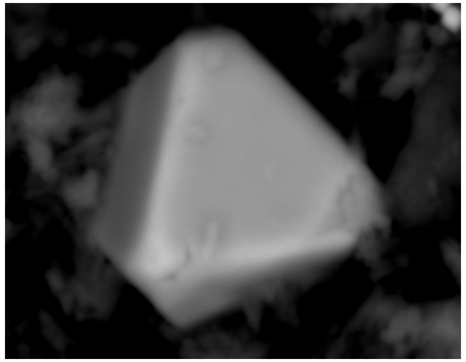
**Dan Leigh**

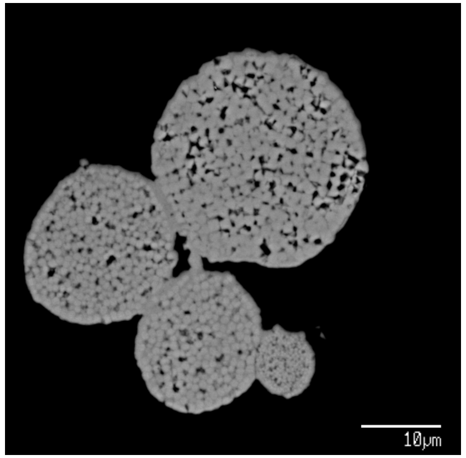
*Battelle Bioremediation Symposium, Austin Texas  May 11, 2023*

# Iron-Sulfide Minerals Occur in Several Forms

## Scanning Electron Microscopy (SEM) Images

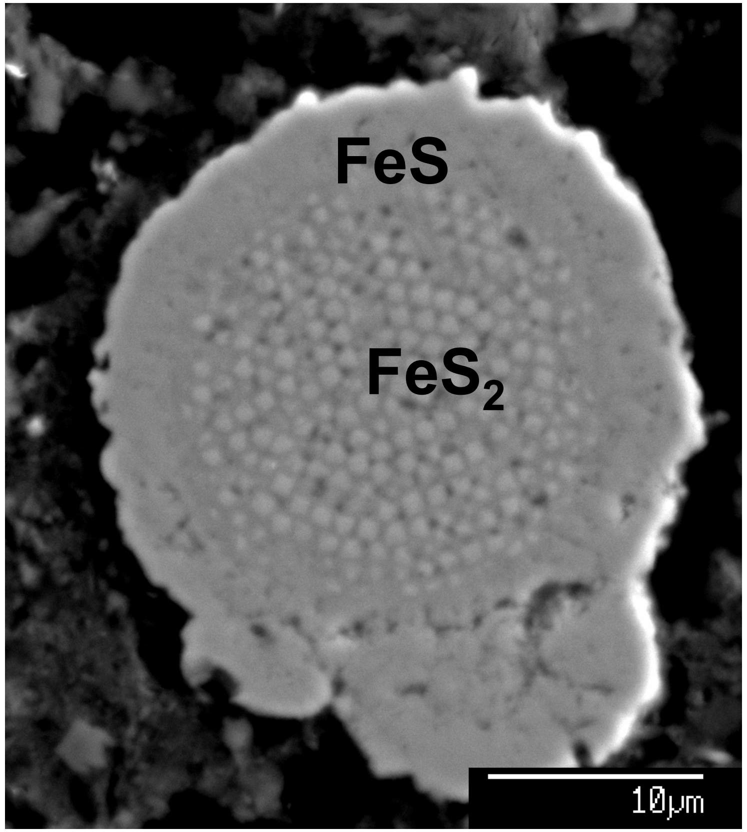
**Euhedral Pyrite ($FeS_2$)**



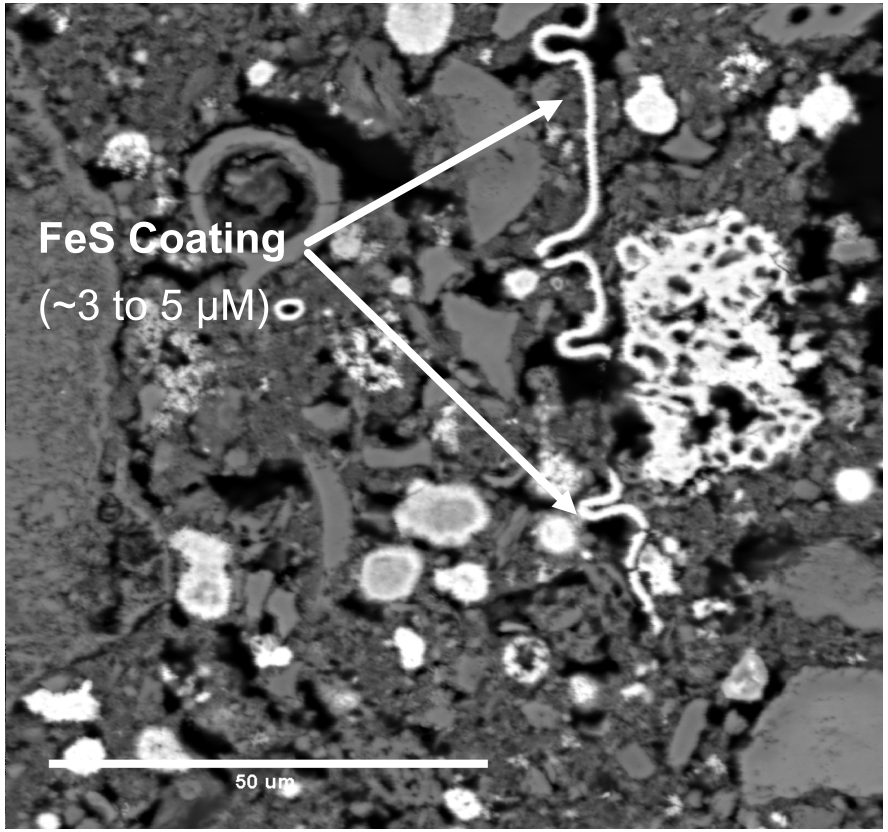


**Framboidal Pyrite ($FeS_2$)**

**Framboidal $FeS_2$ and FeS Coating**



**Fe replacement, FeS coating and nano scale $FeS_2$**



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# Mintrap™ samples from
## EHC® and GeoForm™ ER Application


New Mintrap

Upgradient well
No Treatment

EHC®
(+ ambient sulfate)

GeoForm™ ER

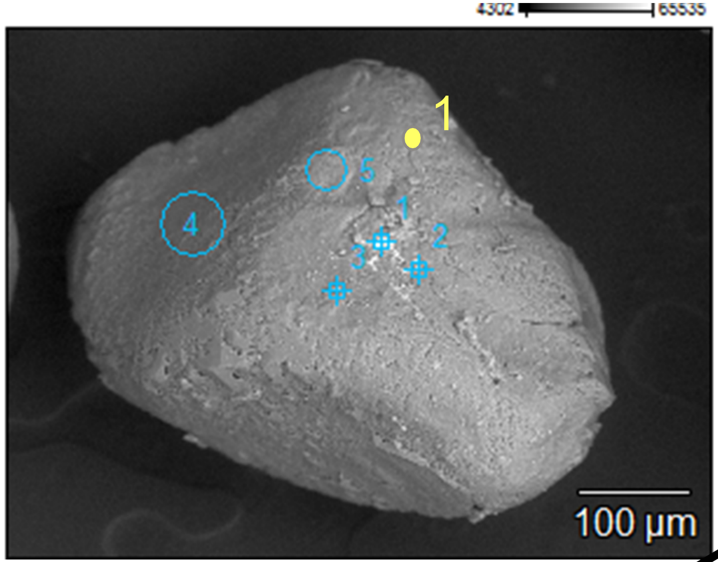
Ulrich, S., Martin Tilton, J., Justicia-Leon, S., Liles, D., Prigge, R., Carter, E., Divine, C., Taggart, D., & Clark, K. (2021). ***Laboratory and initial field testing of the Min-Trap™ for tracking reactive iron sulfide mineral formation during in situ remediation. Remediation. 1–14***. https://doi.org/10.1002/rem.21681

# SEM-EDS Results
# Following GeoForm™ ER Application

Scanning Electron Microscopy (SEM)-Energy Dispersive Spectroscopy (EDS)

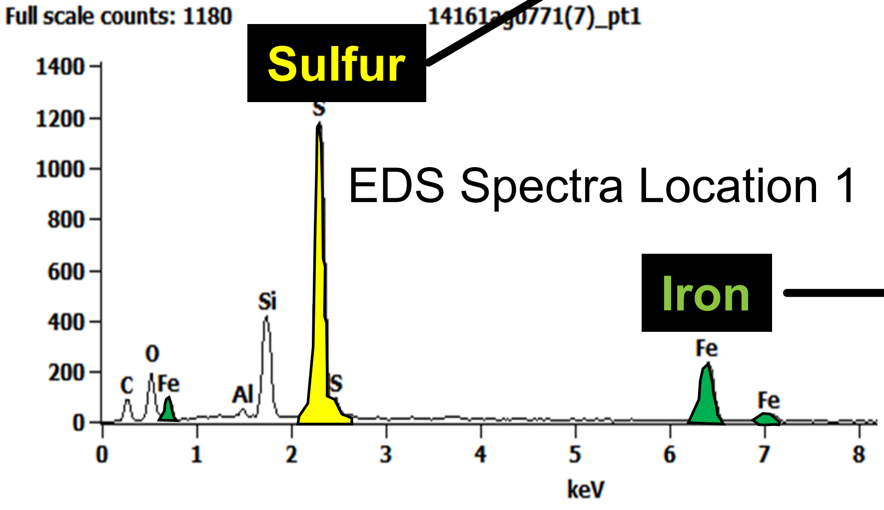
**AMIBA Results**

| AVS (FeS) | CrES ($FeS_2$) |
|---|---|
| 51% | 49% |

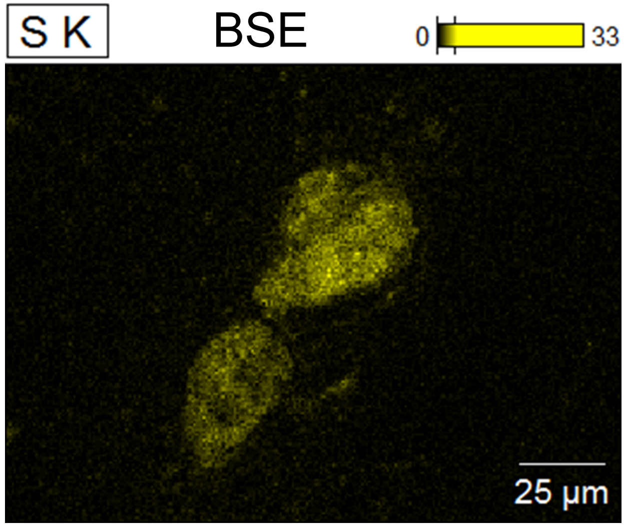


SE EDS Location map

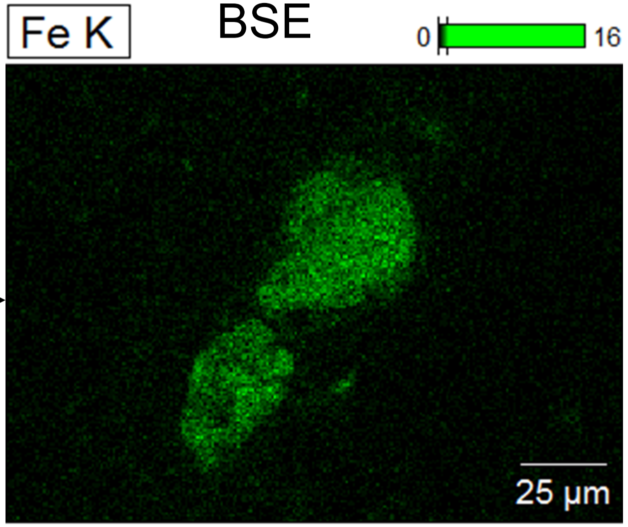
(SE – Secondary Electrons – Show Morphology)



EDS Spectra Location 1



(BSE – Backscatter Electrons)
(Identifies Elements on Surface)



BSE

X-ray overlay map
red = Si,
green = Fe,
yellow = S.

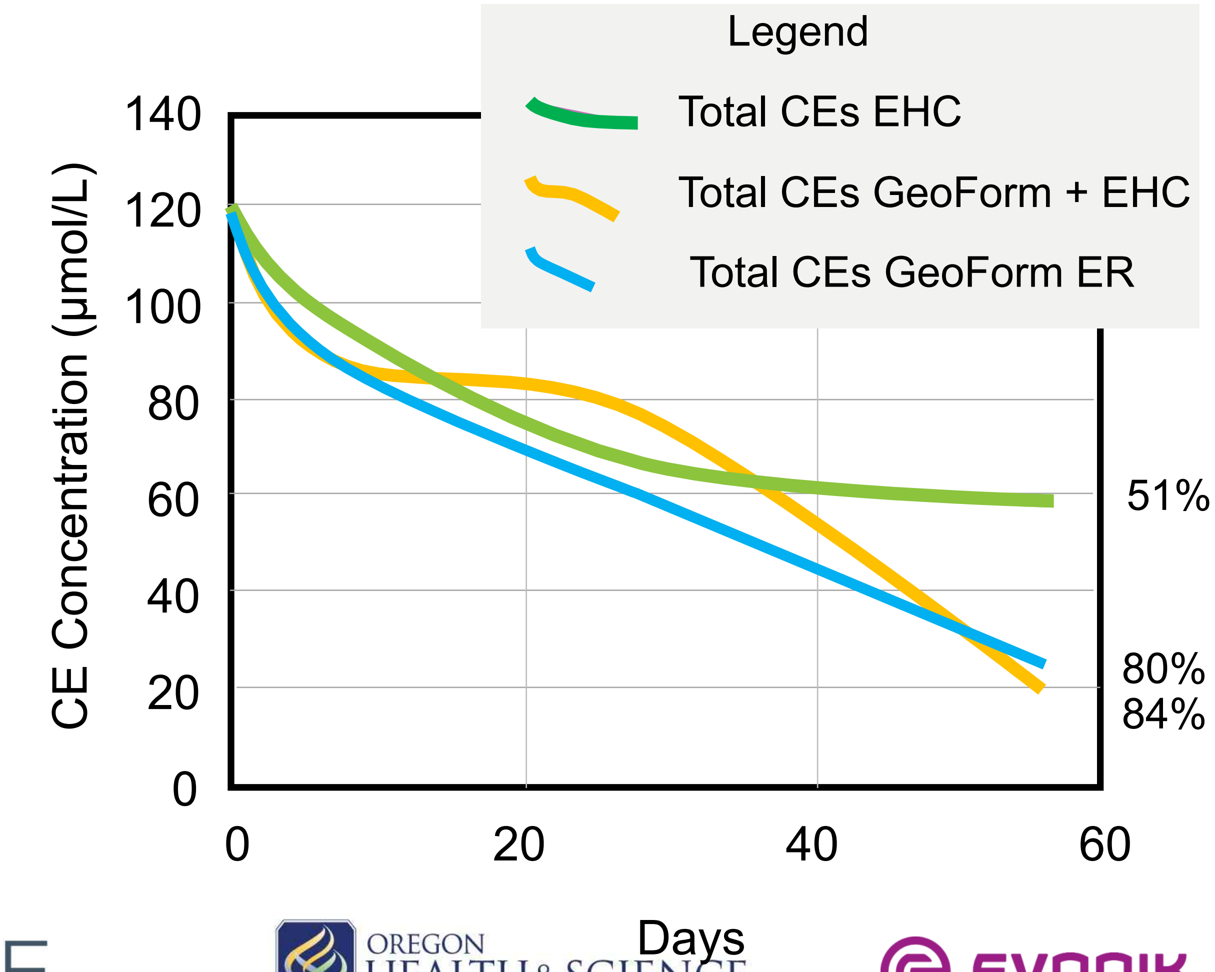
# Case Study: Combined ISCR + BGCR for Treatment of High CE Concentration

## GeoForm® Extended Release Increases EHC® Degradation Rates

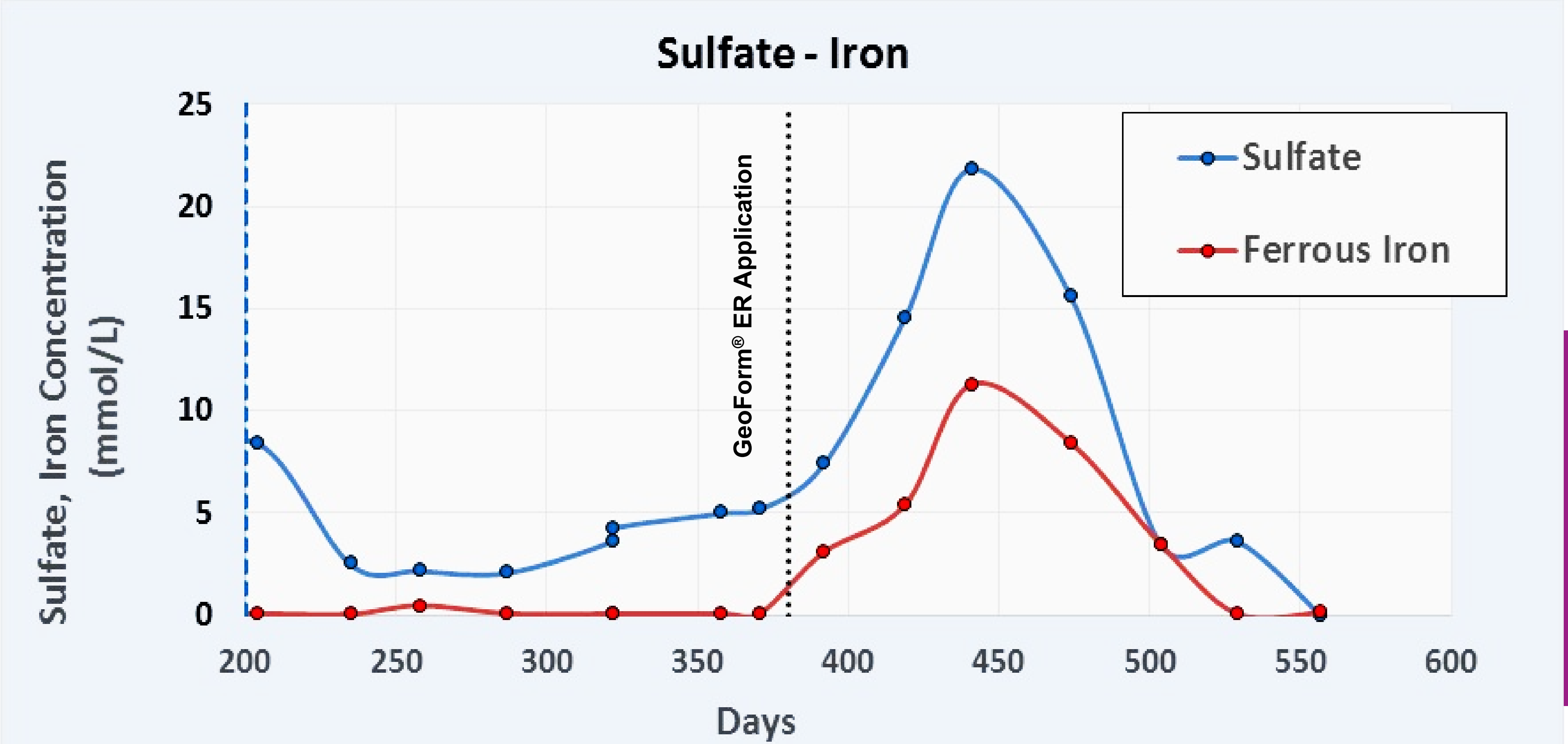
**Addition of GeoForm® Extended Release Increased degradation rate ~63% Relative to EHC® (ISCR) (with sulfate).**

**Results are similar with or without bioaugmentation.**

## Batch Test Results



# Confirming Reagent Distribution Geoform® ER



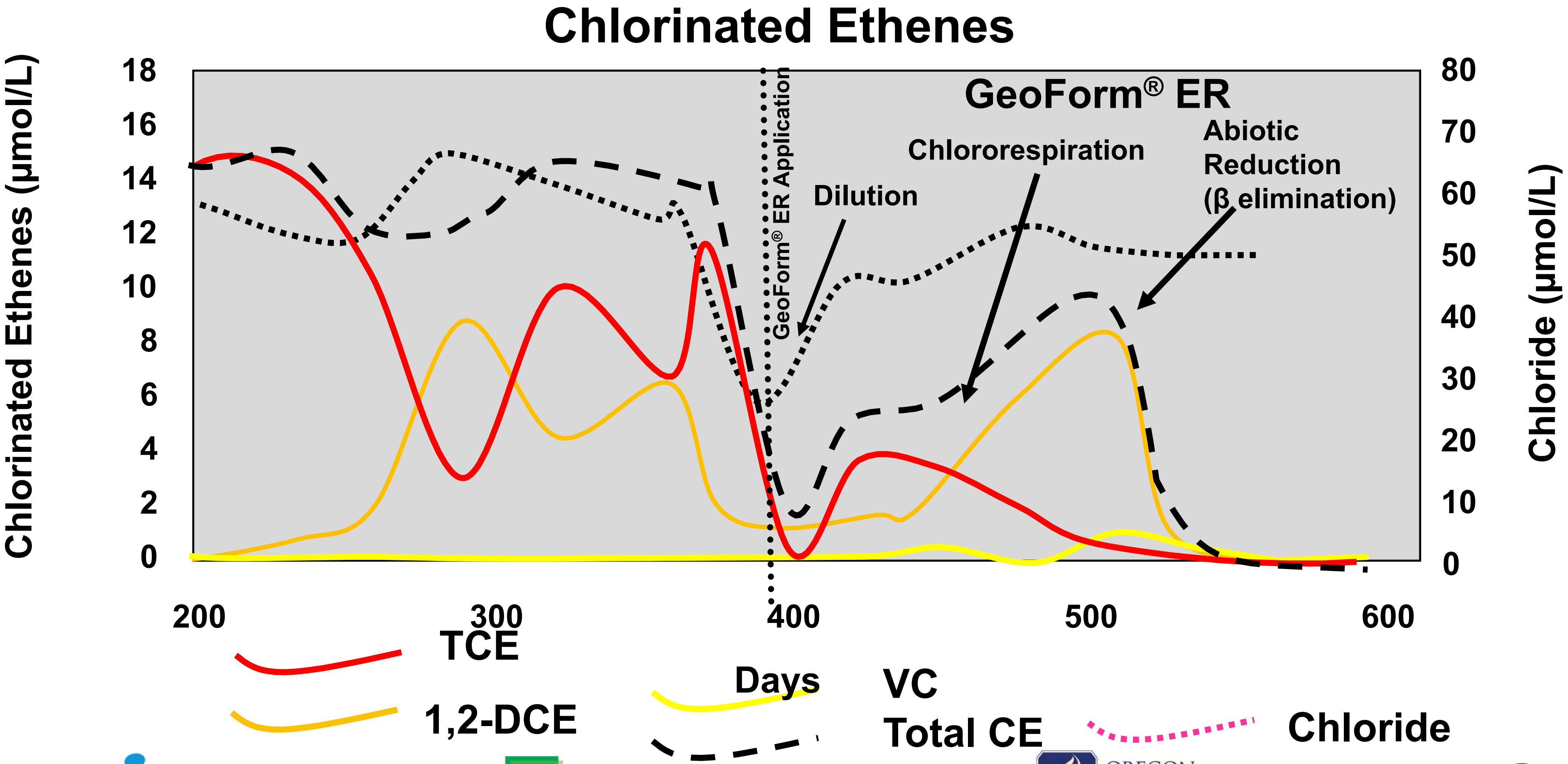
Sulfate FW = 96 Iron FW = 55

**Sulfate and Iron Confirm Reagent distribution**

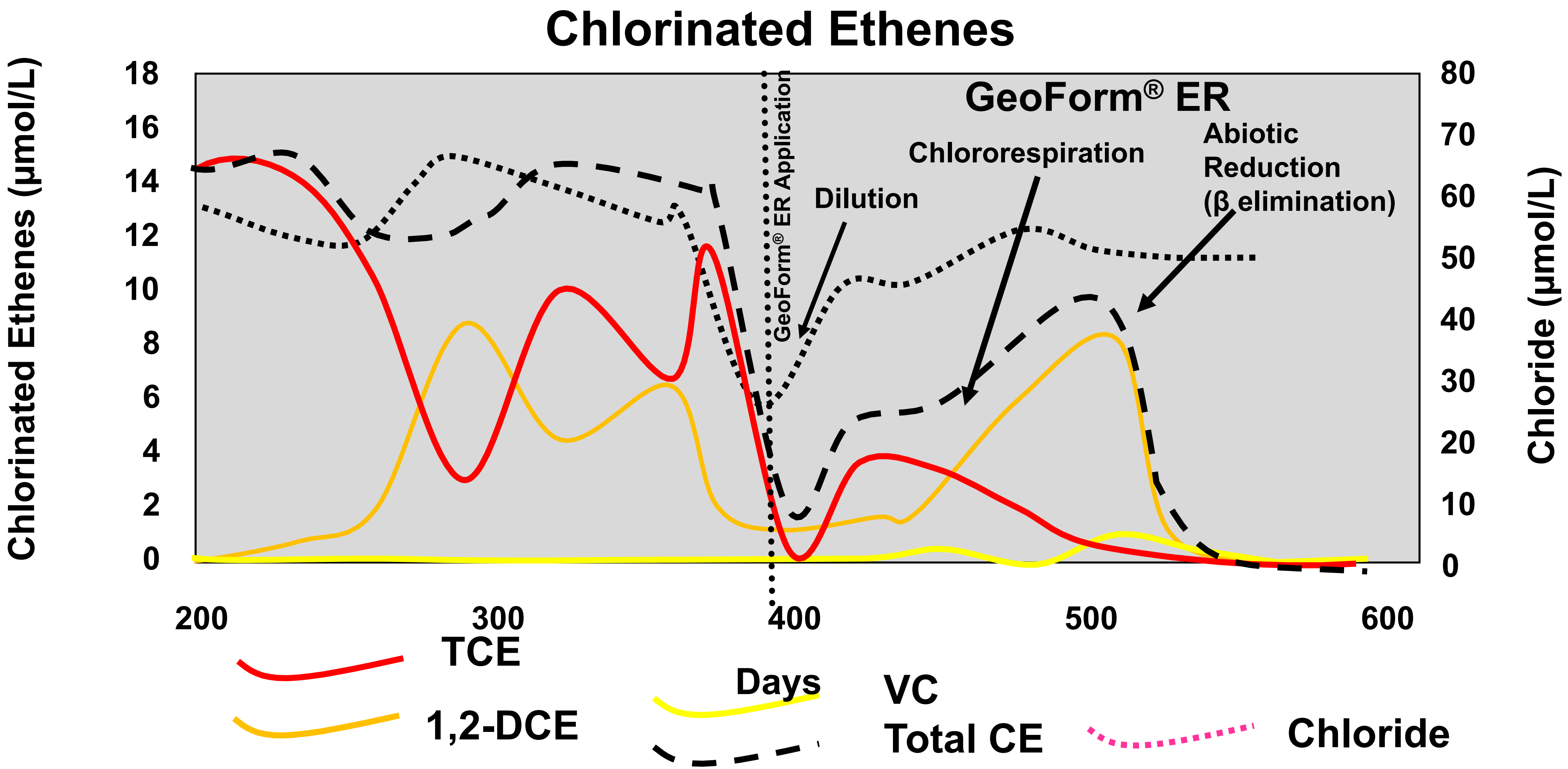
**GEOFORM® Extended Release**

# Case Study: BGCR Treatment of Mixed Chlorinated Organics

GeoForm® ER Treats Mixed CEs, CA and CMs

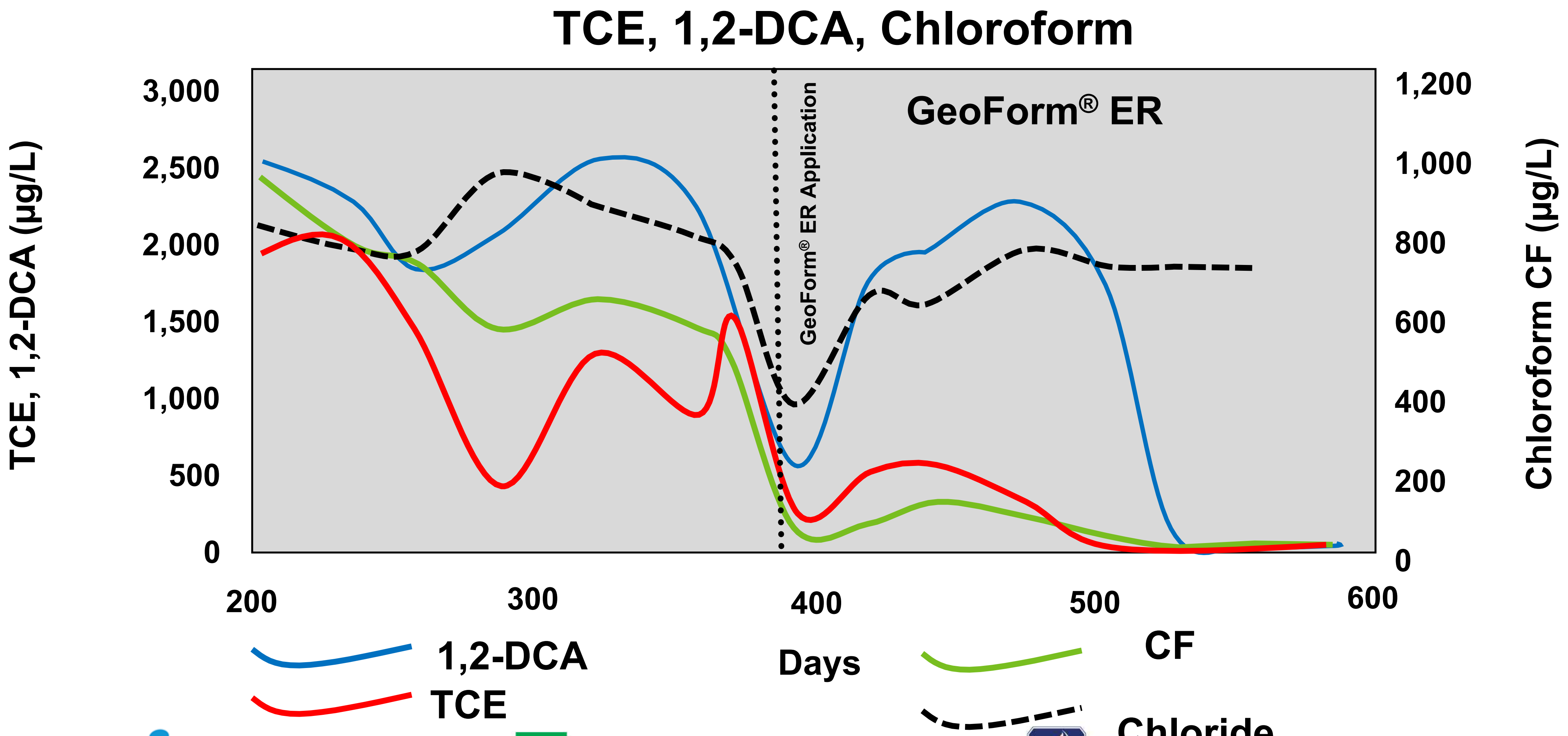


# Not all contaminant reduction is degradation



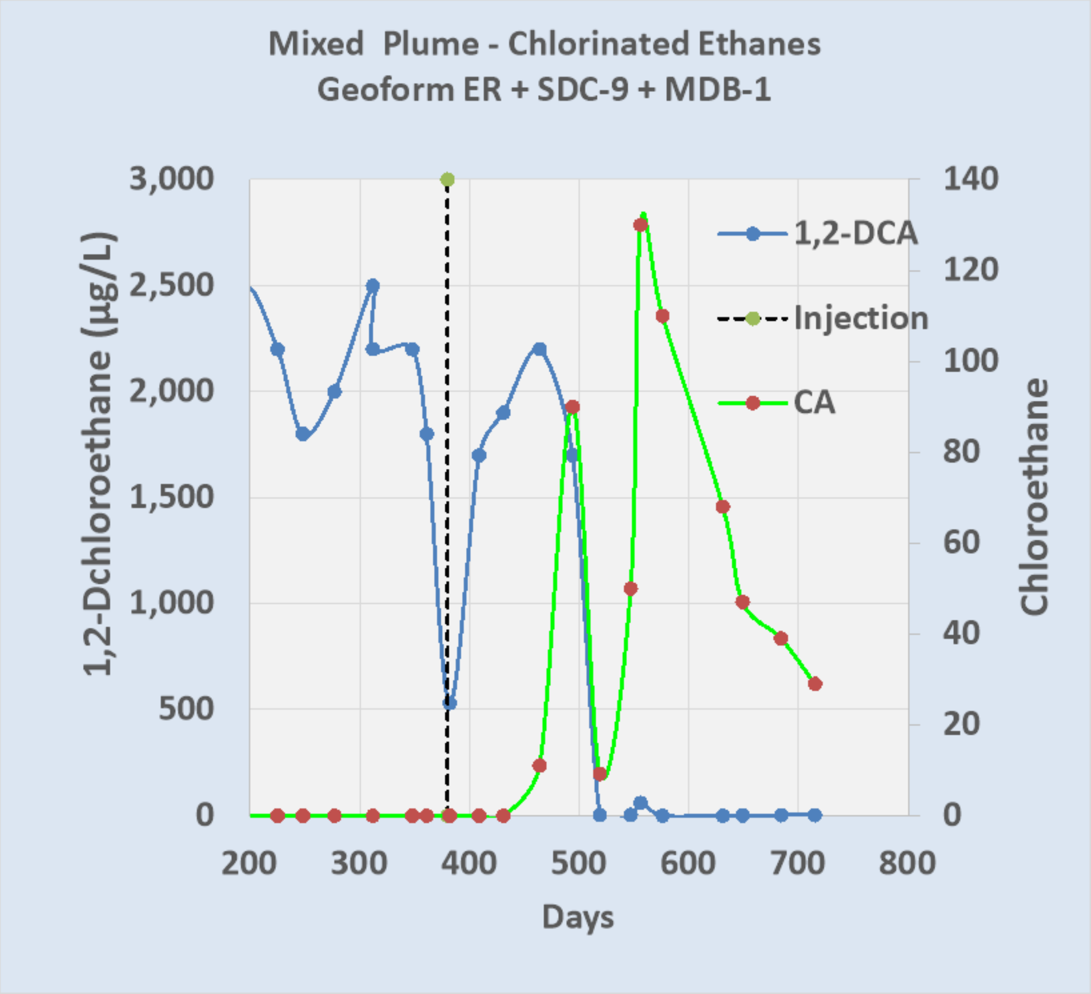
# Case Study: BGCR Treatment of Mixed Chlorinated Organics

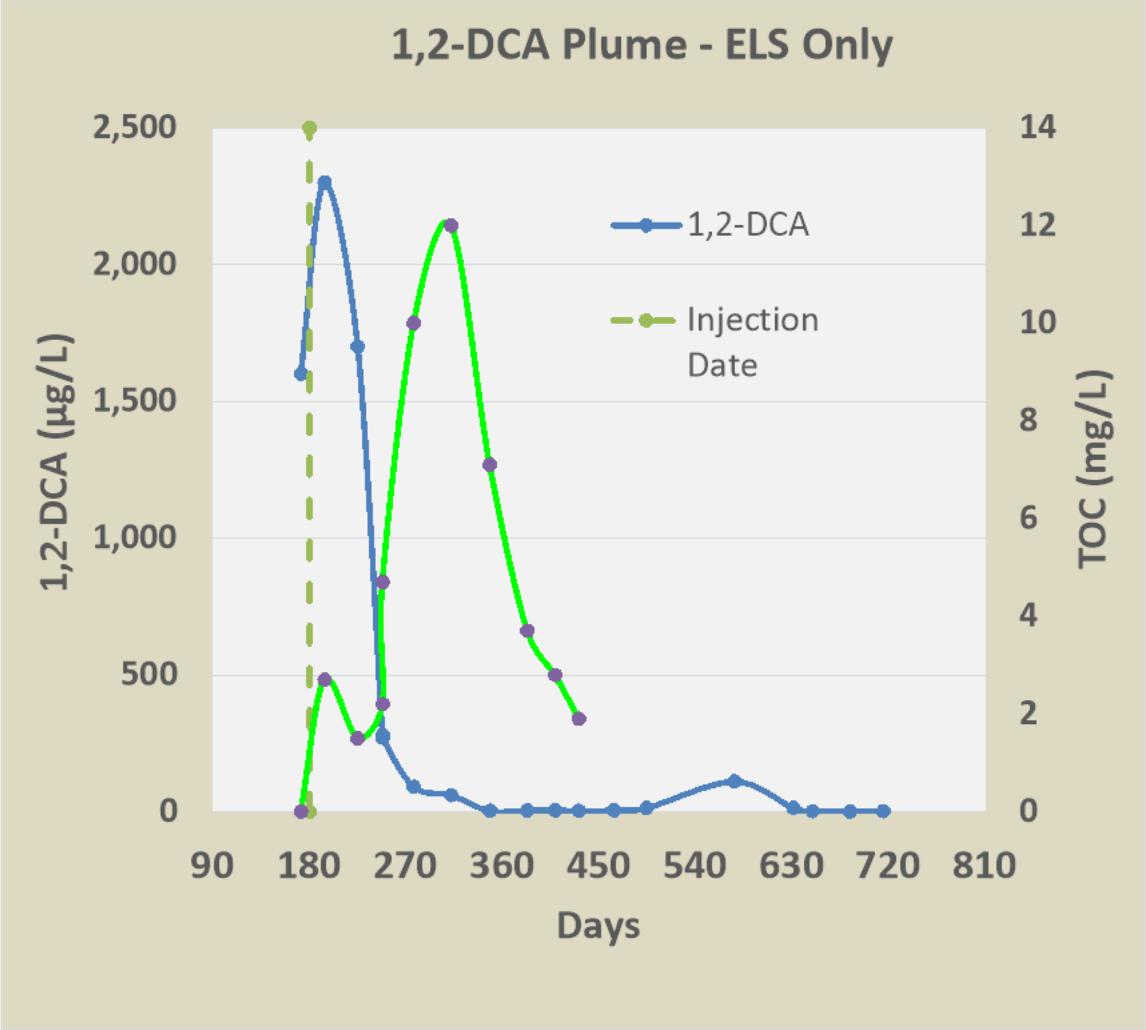
## GeoForm® ER Treats Mixed CEs, CA and CMs



# Degradation of Chlorinated Ethanes

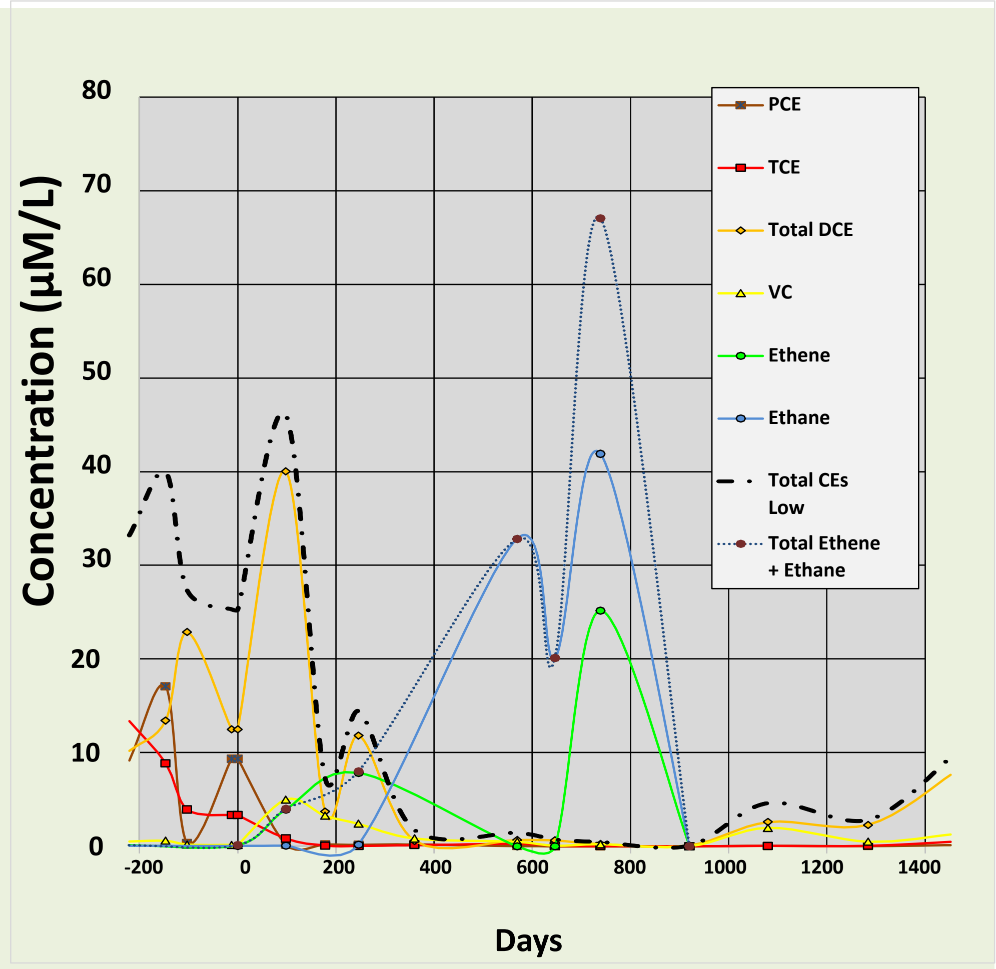
## Geoform ® ER Application

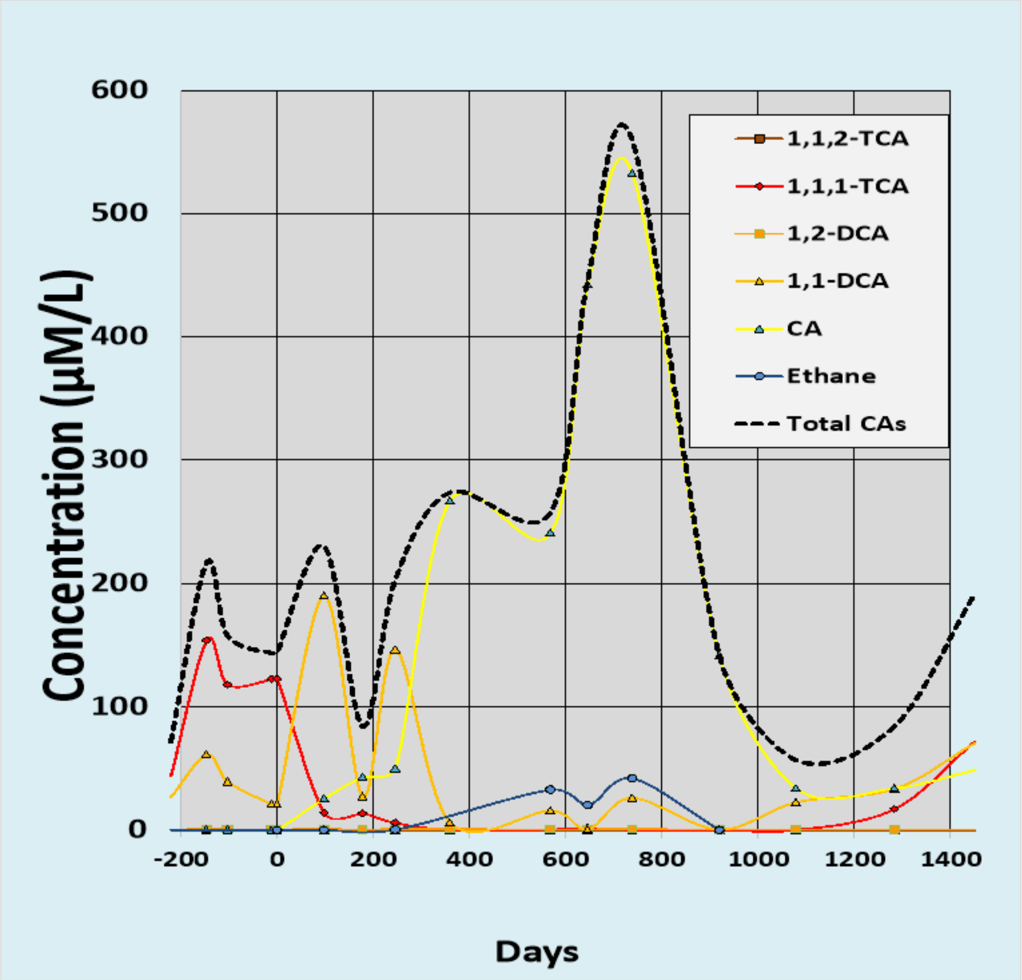




# Degradation of Combined Chlorinated Ethenes and Ethanes

## Geoform ® Soluble Application





# Questions?

[

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# Open discussion

- Please come to a microphone
- Specify which speaker (or the entire panel) you are directing your question
- Clearly state your question

# Science, Application, Monitoring, and Illustrative Case Studies of Biogeochemical Remediation






**Brant Smith**, P.E., Ph.D (Evonik) -- Moderator

**Paul G. Tratnyek**, Ph.D. (Oregon Health & Science University)

**Alan Seech**, Ph.D. (Evonik)

**Dora Taggart** (Microbial Insights)

**Dan Leigh**, PG (Evonik)

**Eric Moskal** (Cascade)

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# Issues for Discussion

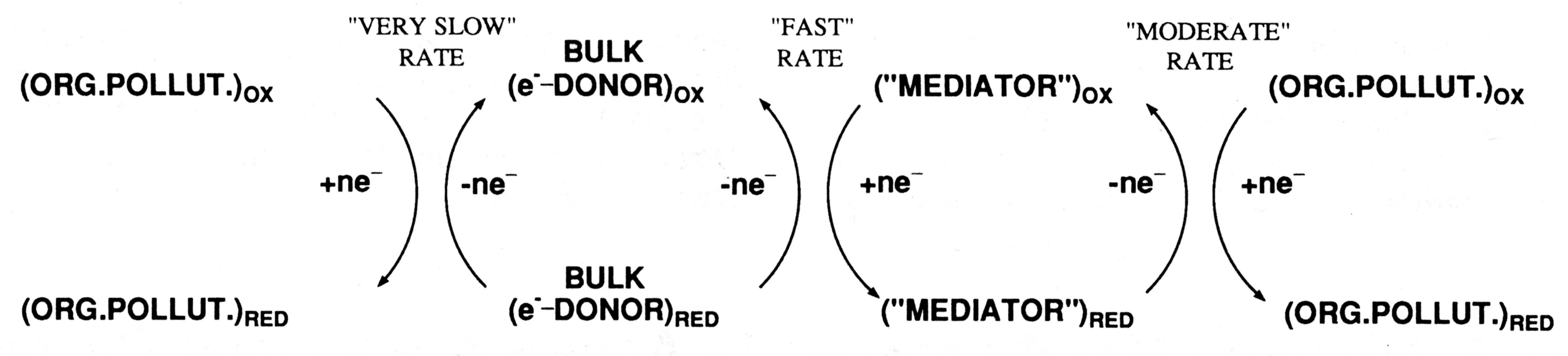
1. Does it matter if Reactive Minerals (RMIs) are formed biotically or abiotically?
2. RMIs might have high reactivity, but isn’t their *capacity* necessarily low?
3. Will there ever be practical ways to directly assay for RMIs in situ?
4. Can abiotic natural attention be significant in the absences of sulfides (i.e., by iron alone)?
5. More
6. More
7. More
8. Where should research be focused to improve BGC?

# Reactive Mineral (Intermediate) Phases

## Mediator Models in General

Paul Tratnyek
tratnyek.org

Dunnivant, Schwarzenbach, Macalady (1992) Figure 1



*Direct* ⟷ *Indirect (Mediated)*

NACs, HCA, CT
~~TCE~~, ~~DCE~~

Microbiology,
ZVI, Dithionite
1° Minerals

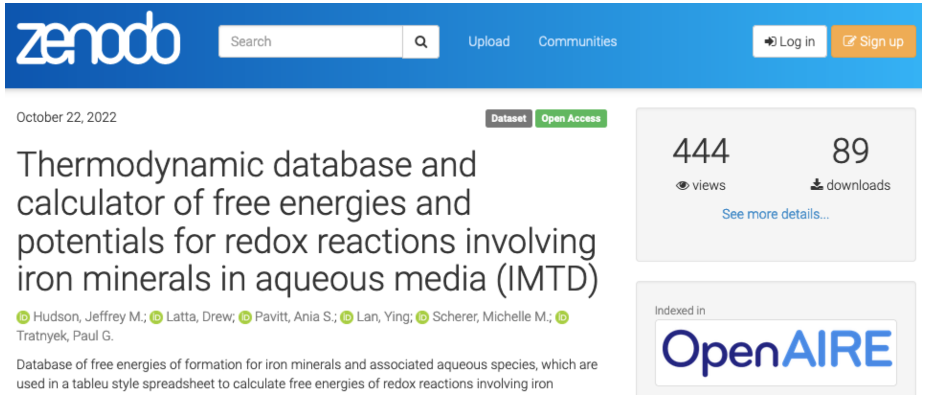
2° Minerals
(RMIs, RAMPs),
NOM, B12, etc.

NACs, HCA, CT
TCE?, DCE?

# Reactive Mineral (Intermediate) Phases

## Evaluating candidate phases

- Iron Mineral Thermodynamic Database
  - ☐ Compiled and compared $\Delta G_f$ data for phases
  - ☐ Calculate $\Delta G_{rxn}$ (standard and formal)
  - ☐ Open access at **https://zenodo.org**

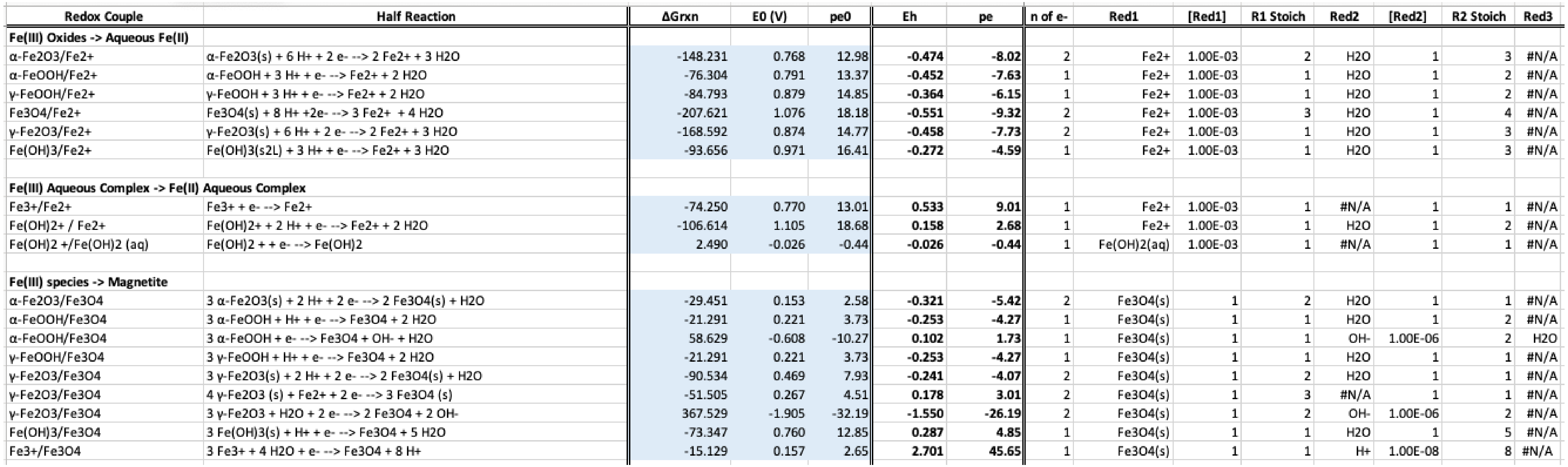


October 22, 2022

Thermodynamic database and calculator of free energies and potentials for redox reactions involving iron minerals in aqueous media (IMTD)

Hudson, Jeffrey M.; Latta, Drew; Pavitt, Ania S.; Lan, Ying; Scherer, Michelle M.; Tratnyek, Paul G.

Database of free energies of formation for iron minerals and associated aqueous species, which are used in a tableu style spreadsheet to calculate free energies of redox reactions involving iron



| Redox Couple | Half Reaction | ΔGrxn | E0 (V) | pe0 | Eh | pe | n of e- | Red1 | [Red1] | R1 Stoich | Red2 | [Red2] | R2 Stoich | Red3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Fe(III) Oxides -> Aqueous Fe(II)** | | | | | | | | | | | | | | |
| α-Fe2O3/Fe2+ | α-Fe2O3(s) + 6 H+ + 2 e- --> 2 Fe2+ + 3 H2O | -148.231 | 0.768 | 12.98 | **-0.474** | **-8.02** | 2 | Fe2+ | 1.00E-03 | 2 | H2O | 1 | 3 | #N/A |
| α-FeOOH/Fe2+ | α-FeOOH + 3 H+ + e- --> Fe2+ + 2 H2O | -76.304 | 0.791 | 13.37 | **-0.452** | **-7.63** | 1 | Fe2+ | 1.00E-03 | 1 | H2O | 1 | 2 | #N/A |
| γ-FeOOH/Fe2+ | γ-FeOOH + 3 H+ + e- --> Fe2+ + 2 H2O | -84.793 | 0.879 | 14.85 | **-0.364** | **-6.15** | 1 | Fe2+ | 1.00E-03 | 1 | H2O | 1 | 2 | #N/A |
| Fe3O4/Fe2+ | Fe3O4(s) + 8 H+ +2e- --> 3 Fe2+ + 4 H2O | -207.621 | 1.076 | 18.18 | **-0.551** | **-9.32** | 2 | Fe2+ | 1.00E-03 | 3 | H2O | 1 | 4 | #N/A |
| γ-Fe2O3/Fe2+ | γ-Fe2O3(s) + 6 H+ + 2 e- --> 2 Fe2+ + 3 H2O | -168.592 | 0.874 | 14.77 | **-0.458** | **-7.73** | 2 | Fe2+ | 1.00E-03 | 1 | H2O | 1 | 3 | #N/A |
| Fe(OH)3/Fe2+ | Fe(OH)3(s2L) + 3 H+ + e- --> Fe2+ + 3 H2O | -93.656 | 0.971 | 16.41 | **-0.272** | **-4.59** | 1 | Fe2+ | 1.00E-03 | 1 | H2O | 1 | 3 | #N/A |
| | | | | | | | | | | | | | | |
| **Fe(III) Aqueous Complex -> Fe(II) Aqueous Complex** | | | | | | | | | | | | | | |
| Fe3+/Fe2+ | Fe3+ + e- --> Fe2+ | -74.250 | 0.770 | 13.01 | **0.533** | **9.01** | 1 | Fe2+ | 1.00E-03 | 1 | #N/A | 1 | 1 | #N/A |
| Fe(OH)2+ / Fe2+ | Fe(OH)2+ + 2 H+ + e- --> Fe2+ + 2 H2O | -106.614 | 1.105 | 18.68 | **0.158** | **2.68** | 1 | Fe2+ | 1.00E-03 | 1 | H2O | 1 | 2 | #N/A |
| Fe(OH)2 +/Fe(OH)2 (aq) | Fe(OH)2 + + e- --> Fe(OH)2 | 2.490 | -0.026 | -0.44 | **-0.026** | **-0.44** | 1 | Fe(OH)2(aq) | 1.00E-03 | 1 | #N/A | 1 | 1 | #N/A |
| | | | | | | | | | | | | | | |
| **Fe(III) species -> Magnetite** | | | | | | | | | | | | | | |
| α-Fe2O3/Fe3O4 | 3 α-Fe2O3(s) + 2 H+ + 2 e- --> 2 Fe3O4(s) + H2O | -29.451 | 0.153 | 2.58 | **-0.321** | **-5.42** | 2 | Fe3O4(s) | 1 | 2 | H2O | 1 | 1 | #N/A |
| α-FeOOH/Fe3O4 | 3 α-FeOOH + H+ + e- --> Fe3O4 + 2 H2O | -21.291 | 0.221 | 3.73 | **-0.253** | **-4.27** | 1 | Fe3O4(s) | 1 | 1 | H2O | 1 | 2 | #N/A |
| α-FeOOH/Fe3O4 | 3 α-FeOOH + e- --> Fe3O4 + OH- + H2O | 58.629 | -0.608 | -10.27 | **0.102** | **1.73** | 1 | Fe3O4(s) | 1 | 1 | OH- | 1.00E-06 | 2 | H2O |
| γ-FeOOH/Fe3O4 | 3 γ-FeOOH + H+ + e- --> Fe3O4 + 2 H2O | -21.291 | 0.221 | 3.73 | **-0.253** | **-4.27** | 1 | Fe3O4(s) | 1 | 1 | H2O | 1 | 1 | #N/A |
| γ-Fe2O3/Fe3O4 | 3 γ-Fe2O3(s) + 2 H+ + 2 e- --> 2 Fe3O4(s) + H2O | -90.534 | 0.469 | 7.93 | **-0.241** | **-4.07** | 2 | Fe3O4(s) | 1 | 2 | H2O | 1 | 1 | #N/A |
| γ-Fe2O3/Fe3O4 | 4 γ-Fe2O3 (s) + Fe2+ + 2 e- --> 3 Fe3O4 (s) | -51.505 | 0.267 | 4.51 | **0.178** | **3.01** | 2 | Fe3O4(s) | 1 | 3 | #N/A | 1 | 1 | #N/A |
| γ-Fe2O3/Fe3O4 | 3 γ-Fe2O3 + H2O + 2 e- --> 2 Fe3O4 + 2 OH- | 367.529 | -1.905 | -32.19 | **-1.550** | **-26.19** | 2 | Fe3O4(s) | 1 | 2 | OH- | 1.00E-06 | 2 | #N/A |
| Fe(OH)3/Fe3O4 | 3 Fe(OH)3(s) + H+ + e- --> Fe3O4 + 5 H2O | -73.347 | 0.760 | 12.85 | **0.287** | **4.85** | 1 | Fe3O4(s) | 1 | 1 | H2O | 1 | 5 | #N/A |
| Fe3+/Fe3O4 | 3 Fe3+ + 4 H2O + e- --> Fe3O4 + 8 H+ | -15.129 | 0.157 | 2.65 | **2.701** | **45.65** | 1 | Fe3O4(s) | 1 | 1 | H+ | 1.00E-08 | 8 | #N/A |

# Reactive Mineral (Intermediate) Phases

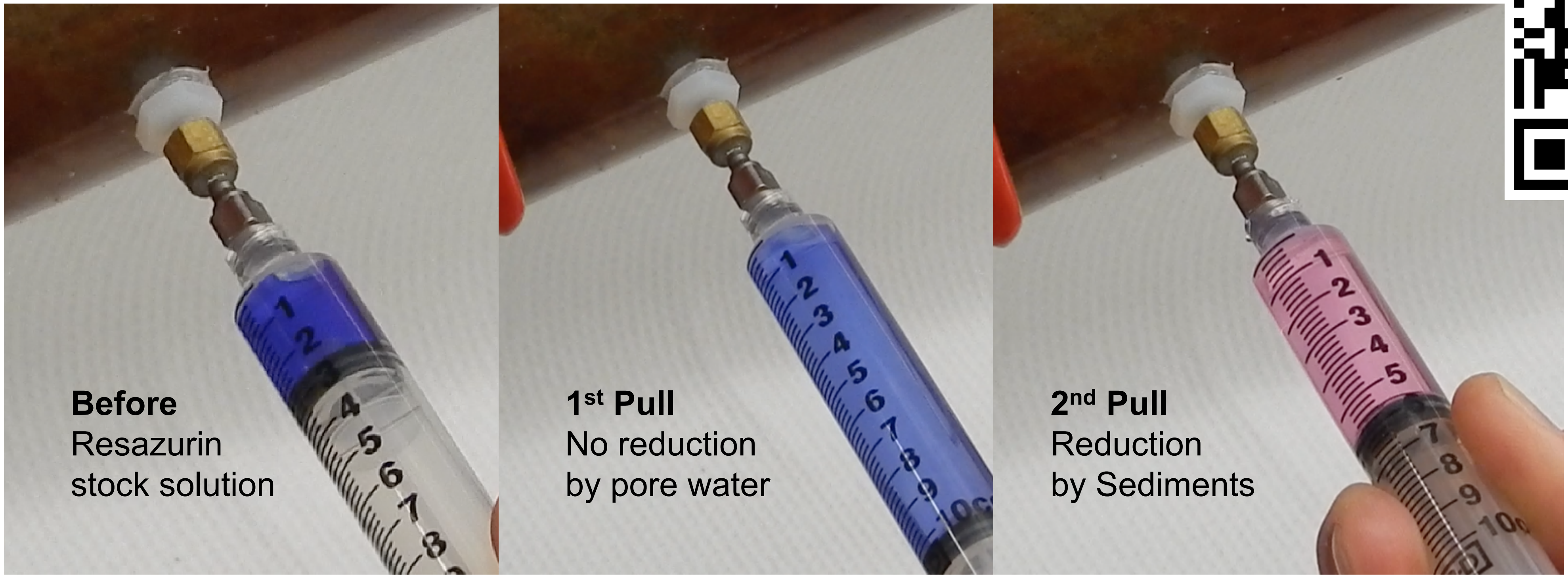
## Reductant is (on) the mineral surface

Paul Tratnyek
tratnyek.org
OHSU

SERDP ER-2308 (Tratnyek and Johnson)

- Not reflected in remote solution phase measurements (e.g., ORP)
- Chemical reactivity probe (CRP) like resazurin shows reactivity
- Resazurin: (1) purple = oxidized, (2) pink = reduced.

**YouTube Video**



**Before**
Resazurin
stock solution

**1st Pull**
No reduction
by pore water

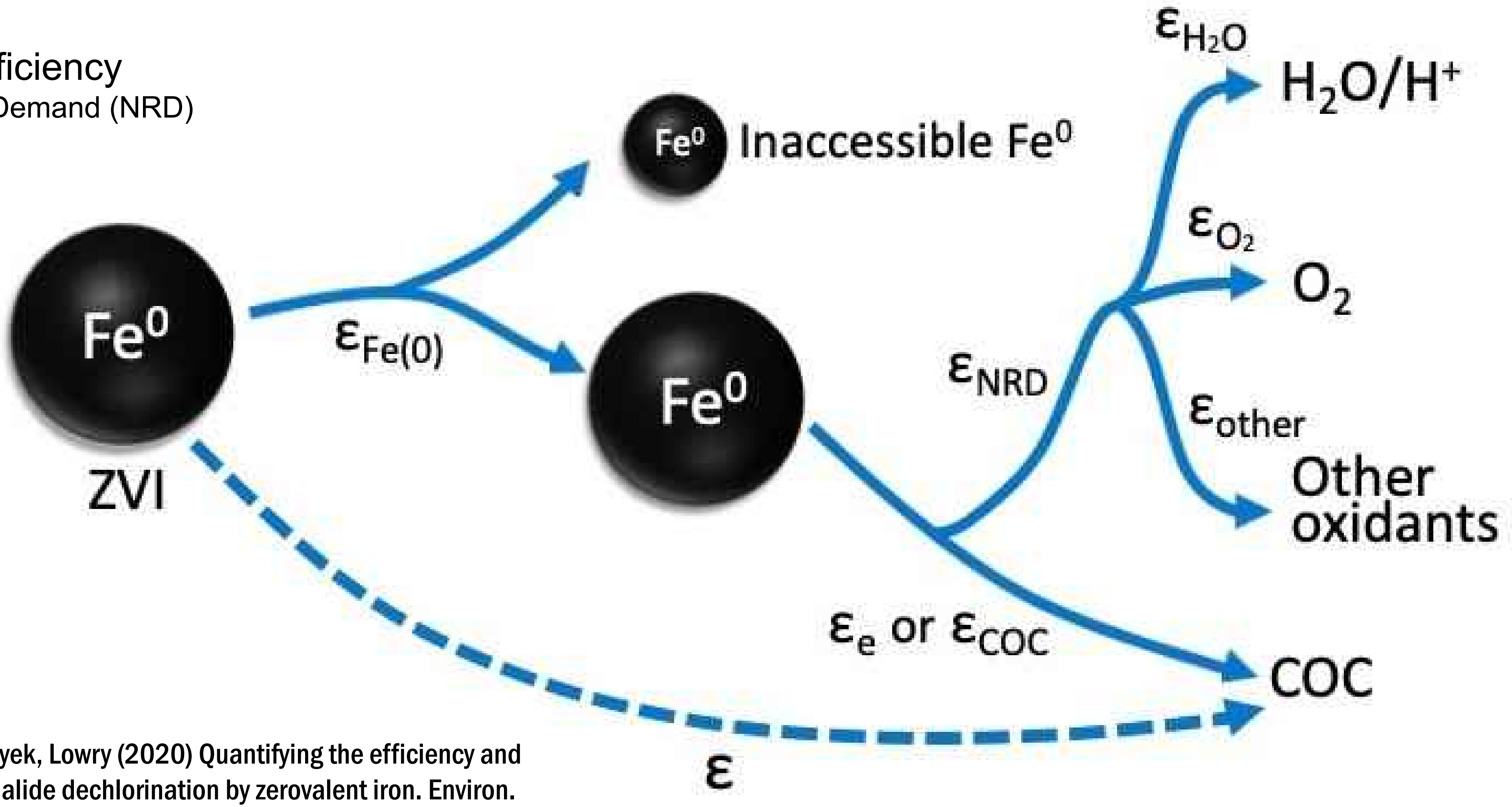
**2nd Pull**
Reduction
by Sediments

# Processes Competing for Reduction

## ZVI as and example

Paul Tratnyek
tratnyek.org

Capacity vs. Efficiency
Natural Reductant Demand (NRD)



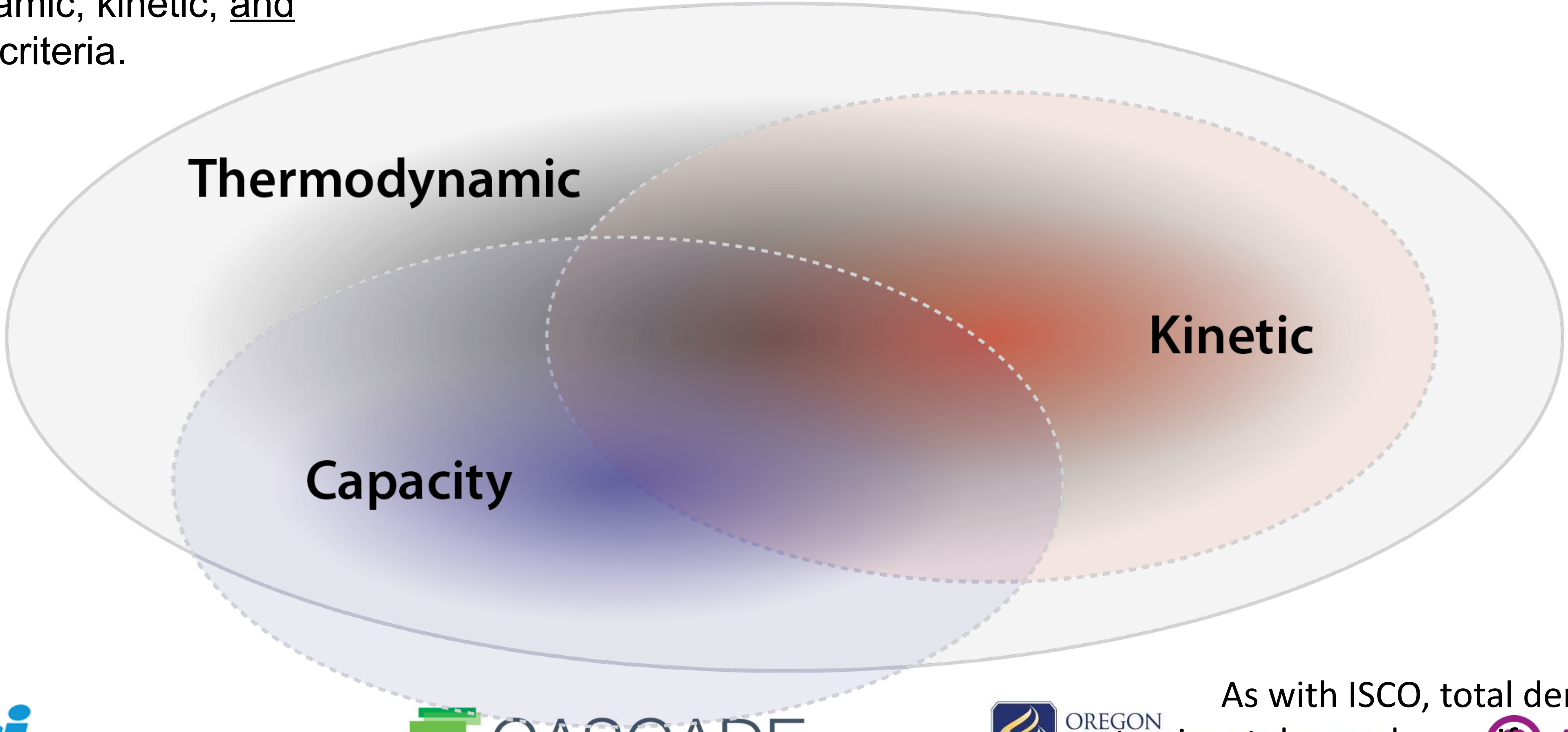
He, Gong, Fan, Ttratnyek, Lowry (2020) Quantifying the efficiency and selectivity of organohalide dechlorination by zerovalent iron. Environ. Sci. Proc. Impacts 22(3): 528-542.

# Requirements for Adequate Degradation

## Three distinct but overlapping criteria

Overall success requires meeting thermodynamic, kinetic, and “capacity” criteria.

SERDP ER-2308 (Tratnyek, Johnson)



As with ISCO, total demand = contaminant demand + aquifer demand

# Stability Regions of Soluble Iron Species in the Presence of Free Sulfide

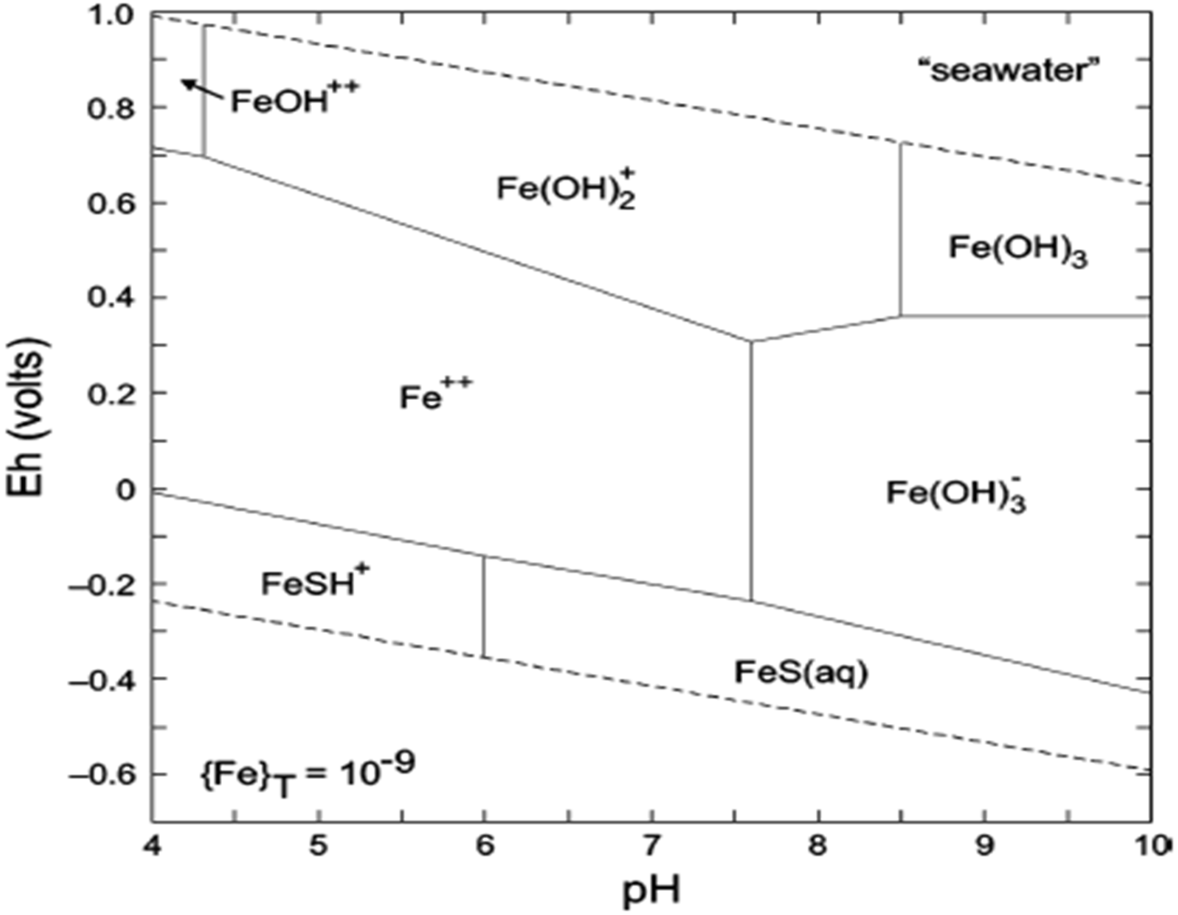


**Figure 14.** pH—Eh diagram of the relative stability of the inorganic dissolved Fe species in an inorganic solution with an average seawater composition and a total dissolved Fe(II) activity of $10^{-9}$.

A different way to look at soluble iron and iron sulfides